







PRACTICAL METHODS OF  
ELECTRO-CHEMISTRY



*BY THE SAME AUTHOR*

**QUALITATIVE CHEMICAL ANALYSIS**  
**(Organic and Inorganic)**

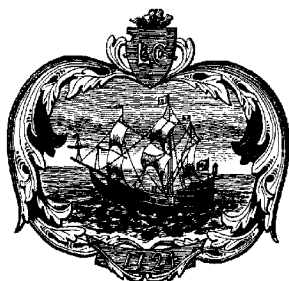
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PRACTICAL METHODS  
OF  
ELECTRO-CHEMISTRY

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IN THE TEXT

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1905

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DEDICATED TO  
SIR JOSEPH SWAN, D.Sc., F.R.S.  
FIRST PRESIDENT OF THE FARADAY SOCIETY



## PREFACE

THE reasons for writing this book—the first of its kind published in this country—have been twofold. In the first place, I have felt the want of such a book for my own students. In the second place, the work was undertaken in the hope that interest in electro-chemistry might be stimulated.

The book has been some years in preparation, owing to the fact that I did not wish to include any experimental work which had not been personally tested or supervised. With a few exceptions—in the separation of the metals—all the experimental work has been carried out in the laboratories of the Borough Polytechnic Institute. All the possible methods of analysis have not been given, but those included have been found to give the best results. Many of the analytical methods are superior, in the ease with which they may be carried out and in accuracy, to ordinary chemical methods; others still leave a good deal to be desired.

The preparations have all been carefully worked out, and I hope that those who work through this book may be stimulated to carry out research in connection with electro-chemical problems.

For help in carrying out the experimental part of the work, I desire most heartily to thank Messrs. A. Fontana, H. B. Law, B.Sc., and W. C. Prebble. For drawing the majority of the diagrams, my thanks are due to Mr. W. C. Prebble; and, for reading the proofs and helping to check the very numerous

references, to Mr. N. J. Bluman. I am also much indebted to Dr. W. Semple for kindly reading through the introductory parts of the book.

I am obliged to Messrs. Baird & Tatlock, London, for kindly lending the block of Fig. 50; to Messrs. Nalder Brothers & Thompson, for Fig. 13; to the Electrical Power Storage Co., for Fig. 33; to Messrs. Sherard, Cowper Coles, & Co., for Figs. 43, 44, 55, and 56; and to Messrs. Longmans, Green & Co., for the engraving of Faraday.

I shall be most obliged for any criticisms, hints, or suggestions from those who use this book.

F. M. P.

LONDON,  
*December 20, 1904.*

## HINTS TO STUDENTS

EXPERIENCE shows that there is a great tendency among those who commence the study of electro-chemistry to *slop* through the work. The average student seems to think all that is necessary is to mix his solutions in a more or less accurate manner, and then to switch on the current—the electricity will do the rest. A greater mistake could not be made; unless details of current density, electromotive force, temperature and composition of the electrolyte are carefully attended to, the results will not be such as are expected, or as are set out in the book. Students are very apt to say, “It is about right,” or “The results are near enough.” Such workers will never succeed, and do not deserve success.

It is not desirable—except as a severe lesson—for the student to commence the analytical separation of an alloy, after he has analysed, say, copper or nickel. The student should carefully work through the major portion of the analysis of single metals before thinking of attempting separations. It is also desirable to try the several methods given for the analysis of each metal, because different workers, after experience, prefer different methods, *i.e.* one worker obtains better results from a specified method than another.

The time given for the analysis of the metals must only be taken as a guide, because concentration of the electrolyte, temperature, and current density are most important factors,



and variations in these conditions will also cause variations in the time factor, and in the E.M.F.

Absolute cleanliness is essential to correct results; the least trace of grease upon the electrodes may be sufficient to ruin an experiment. Platinum is largely employed in electrochemistry, but the average student, and some very much above the average, look upon platinum as being imperishable. This is a very grave error; platinum requires the most careful usage, and should be handled as if it were—as it is—a precious substance.

In all cases in this book, except where otherwise specially stated, the **Current Density**, C.D., refers to the square decimeter of surface. The flag electrodes preferred by the author usually have a surface of  $\frac{1}{2}$  square decimeter; therefore, if a C.D. of 1 ampere is stated as being required, then only  $\frac{1}{2}$  ampere of current must be employed; a registered current of 1 ampere would represent a C.D. of 2 amperes.

The student is advised, after having made a few analytical determinations, to carry out the analytical and preparative work conjointly.

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## LITERATURE ABBREVIATIONS

<i>Amer. Chem. Journ.</i> . . . .	American Chemical Journal.
<i>Amer. Chem. Soc.</i> . . . .	Journal of the American Chemical Society.
<i>Amer. Journ. of Science and Arts</i>	American Journal of Science and Arts.
<i>Amer. Phil. Soc.</i> . . . .	Proceedings of the American Philosophical Society.
<i>Annalen</i> . . . . .	Liebig's Annalen der Chemie.
<i>Ann. Chem. Pharm.</i> . . . .	Annalen der Chemie und Pharmacie.
<i>Ber.</i> . . . . .	Berichte der Deutschen Chemischen Gesellschaft.
<i>Berg. und Hütten Zeit.</i> . . . .	Berg. und Hüttenmannische Zeitung.
<i>British Assoc. Report</i> . . . .	Report of British Association.
<i>Bull. Soc. Chim.</i> . . . .	Bulletin de la Société Chimique de Paris.
<i>Chem. Central Blatt</i> . . . .	Chemisches Central Blatt.
<i>Chem. News</i> . . . . .	Chemical News.
<i>Chem. Soc.</i> . . . . .	Journal of the Chemical Society.
<i>Chem. Zeitung</i> . . . . .	Chemiker-Zeitung.
<i>Compt. Rendus</i> . . . . .	Comptes Rendus.
<i>D. R. P.</i> . . . . .	German Patent.
<i>Electro-chem. and Met.</i> . . . .	Electro-chemist and Metallurgist.
<i>Electrochem. Zeit.</i> . . . .	Electrochemische Zeitschrift.
<i>E. P.</i> . . . . .	English Patent.
<i>Jahrbuch</i> . . . . .	Jahrbuch der Electro-chemie.
<i>Journ. Amer. Electro-chem.</i> . . . .	Journal of the American Electro-chemical Society.
<i>Journ. Anal. Chem.</i> . . . .	Journal of Analytical and Applied Chemistry.
<i>Journ. f. prakt. Chem.</i> . . . .	Journal für praktische Chemie.
<i>Monatsheft</i> . . . . .	Monatsheft für Chemie.
<i>Phil. Mag.</i> . . . . .	Philosophical Magazine.
<i>Phil. Trans.</i> . . . . .	Philosophical Transactions of the Royal Society.
<i>Proc. Royal Soc.</i> . . . . .	Proceedings of the Royal Society.
<i>Soc. Chem. Ind.</i> . . . . .	Journal of the Society of Chemical Industry.
<i>Trans. Faraday Society</i> . . . .	Transactions of the Faraday Society.
<i>U. S. P.</i> . . . . .	American Patent.
<i>Zeit. f. Anal. Chem.</i> . . . .	Zeitschrift für Analytische Chemie.
<i>Zeit. f. Angew. Chem.</i> . . . .	Zeitschrift für Angewandte Chemie.
<i>Zeit. f. Elektrochem.</i> . . . .	Zeitschrift für Elektrochemie.
<i>Zeit. f. Phys. Chem.</i> . . . .	Zeitschrift für Physikalische Chemie.

PART I  
GENERAL



## CHAPTER I.

### *ELECTROLYSIS.*

WHILE electro-chemistry may be said to date back to the discovery of the galvanic element by Volta in 1800, a discovery which led to the isolation of the alkali metals by Davy in 1806, we have to thank Faraday before all others for placing the subject upon a firm and scientific foundation. Not only did Faraday, by formulating the laws governing the passage of the electric current through electrolytes, in 1833, lay the foundation stone of theoretical and practical electro-chemistry; but in 1831 he had already shown that a temporary current is induced in a closed circuit by the movement of a magnet in its neighbourhood—an observation, the application of which in future years was destined to revolutionise many phases of chemical industry, and to found a new branch of engineering, the development of which seems to have no bounds.

### **Electrolysis.**

That some substances, such as metals, conduct electricity readily, and that other substances, such as glass and porcelain, will not allow its passage has been known for a great number of years. Since the time of Volta, it has been recognised that certain liquids may also be classed among conductors of the electrical current.

Faraday called metals and similar substances **conductors of the first class**; liquids he called **conductors of the second class**. We shall not here concern ourselves with the manner in which the electric current passes through a metallic conductor: a

few years ago there was very little controversy as to how this took place—to-day there are several theories. It is, however, necessary to have some conception of the way in which liquids may be supposed to be able to conduct electricity.

All liquids are not conductors; pure water itself is not a conductor. Aqueous solutions of **salts**, **acids**, and **bases** permit the passage of the current; on the other hand, solutions of some substances, such as sugar, gum, etc., do not possess this property. It is therefore obvious that salts, acids, and bases behave differently in solution from other classes of substances.

According to our present conceptions, it is presumed that salts, acids, and bases, when in solution, are not there exclusively in the form of complete molecules, but that the molecules are, in solution, dissociated to a greater or less extent into **ions**. For example, common salt, NaCl, when dissolved in water is supposed to be split up into the positive ion  $\text{Na}^+$ , and the negative ion  $\text{Cl}^-$ . In the solid condition sodium chloride is electrically neutral, having neither a positive nor a negative charge, or, what comes to the same thing, it has opposed charges in equal proportion. In solution, however, some at least of the molecules break up into the ion  $\text{Na}^+$  carrying a heavy positive electrical charge, and the ion  $\text{Cl}^-$  with an equal charge of negative electricity. In a similar manner, potassium hydroxide in solution is split up into the positive ion  $\text{K}^+$ , and the negative ion  $\text{OH}^-$ , known as the hydroxyl ion.<sup>1</sup>

When two pieces of platinum, connected with the opposite poles of an electric battery (these pieces of platinum when so connected are called **electrodes**), are placed in a solution of sodium chloride, a current of electricity passes through the solution, and it is found that chlorine gas is evolved at the piece of platinum connected to the positive pole of the battery, while hydrogen gas is given off at the piece in connection with the negative pole. It has already been stated that pure water will not conduct electricity; how is it, then, that the electric current readily passes

<sup>1</sup> The valency of the cation is represented by a (+): thus in  $\text{Ag}^+$  and in  $\text{Ba}^{++}$ . The valency of the anion is represented thus (-), e.g.  $\text{Cl}^-$  and  $\text{SO}_4^{--}$ .

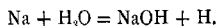
through a solution of sodium chloride? It is a well-known law in electrical science, that like attracts unlike, and like repels like, *i.e.* negatively charged bodies attract positively electrified bodies, and repel negatively electrified bodies. Now, in a solution of sodium chloride there are present  $\text{Cl}^-$  ions carrying a negative electric charge, and  $\text{Na}^+$  ions charged with an equal quantity of positive electricity. It follows that the negative ions will be attracted to the positive pole, and the positive ions to the negative pole. In other words, the electric current will be conveyed across the solution from one pole to the other by the ions. The  $\text{Cl}^-$ , or negative, ions will convey the negative electricity to the positive electrode, where they will become neutralised by the positive electricity at that electrode. The  $\text{Na}^+$ , or positive, ions will convey the positive electricity to the negative electrode, where they will become neutralised by the positive electricity at that pole.

It was Faraday who first called the particle which conveys the current in solutions an **ion**,—from the Greek word meaning wanderer or traveller. He called the ion which conveyed the positive electricity, and therefore appears at the negative pole, the **cation**, and the negative pole the **cathode**. The ion which conveys the negative electricity was designated the **anion**, and the positive pole at which it is neutralised the **anode**.

The ion  $\text{Cl}^-$  is not molecular chlorine as we know it—a yellow gas of unpleasant odour. Neither is the ion  $\text{Na}^+$  molecular sodium—a readily oxidisable metal, which decomposes water. The molecules are electrically neutral; the ions, on the other hand, possess an electric charge—the anion being negatively charged, the cation having an equal positive charge. The moment the ions are liberated at the electrode, *i.e.* have their charges neutralised by an equal quantity of the opposite charge, they become atoms which, uniting together, become molecules of the substances in the free state as we know them. Thus, as soon as the electric current passes through the solution, a smell of chlorine gas is perceptible at the anode, and hydrogen is evolved at the cathode; the solution in the neighbourhood of the cathode becoming



alkaline, owing to the metallic sodium at the moment of its liberation reacting with the water thus—



The production of hydrogen in this example is thus due to a secondary action. An example might, however, be taken in which both the anion and cation, on neutralisation, give rise to the corresponding molecular forms. For instance, in a solution of copper chloride we have the cation  $\text{Cu}^{++}$  and the two anions  $\text{Cl}^-$ , the two anions together bearing the same amount of electricity, but of opposite sign, as the  $\text{Cu}^{++}$  cation. On electrolysing this solution gaseous chlorine makes its appearance at the anode, and *metallic copper is plated on to the cathode.*

According to Le Blanc, leaving out of account metallic salt solutions and salts of the halogens, the electrolysis of water may be looked upon as being a primary decomposition. In water we have  $\text{H}^\cdot$  and  $\text{OH}^\cdot$  ions. Now, the electrical conductivity of a solution is brought about by all the ions in the solution. In electrolysing a solution of potassium sulphate, what we notice is the separation of hydrogen at the cathode, and oxygen at the anode. When therefore the current is not too strong, it is not necessary to assume the separation of potassium at the cathode, and the  $\text{SO}_4$  radical at the anode, although this assumption is usually made. There will always be  $\text{H}^\cdot$  and  $\text{OH}^\cdot$  ions present, since these will be immediately generated by the undissociated water. At the electrode, the action which will take place is naturally that which proceeds the most readily; that is, in this case, the separation of the  $\text{H}$  and  $\text{OH}$  radicals. As a matter of fact, in ordinary electrolysis, when currents of considerable intensity are being used, we may presume that we have both a primary and secondary reaction proceeding simultaneously.

Faraday, in his researches into the phenomena of electrolysis, found by careful measurement that the quantity of substance deposited at the electrodes always corresponded to the amount of electricity which had been passed through the solution. He further found that amount of substance deposited at the cathode

always bore the same ratio to the quantity given up at the anode; further, that the quantity of different elements yielded up at the electrodes by a given current bore a simple ratio to their combining weights. The laws of Faraday, deduced from these facts, are usually formulated as follows:—•

1. *The amount of a substance liberated by the electric current is proportional to the total quantity of electricity passed through the solution.*

2. *By the same quantity of current equivalent proportions of different electrolytes are decomposed. And the amount of different substances deposited is in the ratio of their equivalent weights.*

The first law states that the amount of substance liberated depends upon the quantity of current passed. It does not matter whether the current has been passed slowly or rapidly. For example, in 1 hour a current of 1 ampere will deposit 1.1858 gm. of copper at the cathode, a current of 2 amperes would liberate this quantity in half an hour, and one of half an ampere would require to be passed for 2 hours to deposit the same quantity.

When a current of 1 ampere is passed through a circuit for 1 second, the quantity of electricity which passes is called a **coulomb**; that is, a coulomb is 1 ampere second. A current of 1 ampere passing for 96,540 seconds will deposit the gram equivalent of an element; in other words, 96,540 coulombs of electricity are required to deposit the gram equivalent of an element. This quantity of electricity is sometimes called a **Faraday**. Lehfeltd<sup>1</sup> suggests that the name might be brought into more common use; we will, therefore, in this book employ the term faraday to denote the quantity of electricity 96,540 coulombs. One coulomb will deposit 0.001118 gm. of silver from a solution of a silver salt. If this quantity is divided into the atomic weight of silver, we obtain—

$$\frac{107.93}{0.001118} = 96,538 \text{ coulombs.}$$

Again, 1 coulomb of electricity will deposit 0.0003294 gm. of copper from a solution of a cupric salt, and if this number is

<sup>1</sup> "Electro-chemistry," pt. I. p. 3.

divided into 31.8, the hydrogen equivalent of copper, compared to oxygen as 16, we obtain—

$$\frac{31.8}{0.0003294} = 96,539 \text{ coulombs.}$$

But when 1 coulomb is passed through a solution of a cuprous salt 0.0006588 gm. of copper is deposited. The equivalent in this case is 63.6, the cuprous ion being monovalent,

$$\frac{63.6}{0.0006588} = 96,539 \text{ coulombs.}$$

The last two examples prove Faraday's second law, that the same quantity of current will liberate equivalent proportions of the different elements. The quantity of electricity necessary to liberate 1.008 gm. of hydrogen will liberate 107.93 gm. of silver, 31.8 gm. of copper from cupric salts, and 63.6 gm. of copper from cuprous salts. These examples all refer to substances liberated at the cathode, but the same quantity of current will likewise liberate at the anode 8 gm. of oxygen, 35.45 gm. of chlorine, 126.85 gm. of iodine, etc.

Only the elements most likely to be required in general electro-chemical work have been included in the following table. There is, however, no difficulty in calculating the electro-chemical equivalent of an element. If the atomic weight and the valency are known, then the electro-chemical equivalent is found by, first dividing the atomic weight by the valency number and the number so obtained by 96,540. For example, the atomic weight of boron is

11 (O = 16) and its valency is 3. We therefore get  $\frac{11}{3} = 3.6666$ .

The number 3.6666 is the oxygen equivalent of boron, and from this we obtain—

$$\frac{3.666}{96,540} = 0.003797 \text{ mg.}$$

That is, 0.003797 mg. of boron would be deposited in 1 second by a current of 1 ampere passing through its solutions.

TABLE I.—ATOMIC AND EQUIVALENT WEIGHTS AND ELECTRO-CHEMICAL EQUIVALENTS OF THE ELEMENTS.

Calculated from the table of atomic weights drawn up by the International Committee for 1903.

Element.	Formula and valency.	Atomic weight.		Equivalent weight.		Electro-chemical equivalent.	
		H = 1	O = 16	H = 1	O = 16	Per coulomb in mg. per sec.	Per ampere hr. in grms., i.e. 3600 coulombs.
Aluminium	Al...	26.90	27.10	8.966	9.033	0.09357	0.3368
Antimony	Sb...	119.30	120.20	39.766	40.067	0.41504	1.4941
Arsenic	As...	74.40	75.00	24.800	25.000	0.25896	0.9323
Barium	Ba...	136.40	137.40	68.200	68.700	0.71160	2.5619
Bismuth	Bi...	206.90	208.50	68.966	69.500	0.71992	2.5917
Bromine	Br	79.36	79.96	79.360	79.960	0.82830	2.9818
Cadmium	Cd...	111.60	112.40	55.800	56.200	0.58220	2.0957
Calcium	Ca...	39.80	40.10	19.900	20.050	0.20769	0.7477
Chlorine	Cl	35.18	35.45	35.180	35.450	0.36721	1.3220
Chromium	Cr...	51.70	52.10	25.850	26.050	0.26984	0.9714
"	Cr...	51.70	52.10	17.233	17.367	0.17989	0.6476
Cobalt	Co...	58.56	59.00	29.280	29.500	0.30558	1.1001
Copper	Cu	63.10	63.60	63.100	63.600	0.65880	2.3717
"	Cu...	63.10	63.60	31.550	31.800	0.32940	1.1858
Gold	Au...	195.70	197.20	65.233	65.733	0.68090	2.4513
Hydrogen	H	1.00	1.008	1.000	1.008	0.01044	0.03759
Iodine	I	125.90	126.85	125.900	126.850	1.31400	4.7303
Iron	Fe...	55.50	55.90	27.750	27.950	0.28952	1.0423
"	Fe...	55.50	55.90	18.500	18.633	0.19301	0.6949
Lead	Pb...	205.35	206.90	102.675	103.450	1.07165	3.8580
Lithium	Li	6.98	7.03	6.980	7.030	0.07282	0.26215
Magnesium	Mg...	24.18	24.36	12.090	12.180	0.12626	0.4545
Manganese	Mn...	54.60	55.00	27.300	27.500	0.28486	1.0255
"	Mn...	54.60	55.00	18.200	18.330	0.18991	0.6837
Mercury	Hg...	198.50	200.00	198.500	200.000	2.07170	7.4580
"	Hg...	198.50	200.00	99.250	100.000	1.03590	3.7291
Molybdenum	Mo...	95.30	96.00	47.650	48.000	0.49721	1.7900
Nickel	Ni...	58.30	58.70	29.150	29.350	0.30402	1.0945
Nitrogen	N...	13.93	14.04	4.643	4.680	0.048478	0.17452
Oxygen	O	15.88	16.00	7.940	8.000	0.08287	0.29833
Platinum	Pt...	193.30	194.80	48.325	48.700	0.50446	1.8160
Potassium	K	38.86	39.15	38.860	39.150	0.40550	1.4598
Silver	Ag	107.12	107.93	107.120	107.93	1.11800	4.0248
Sodium	Na...	22.88	23.05	22.880	23.050	0.23876	0.8596
Strontium	Si...	86.94	87.80	43.470	43.900	0.45371	1.6333
Tin	Sn...	118.10	119.00	59.050	59.500	0.61630	2.2188
"	Sn...	118.10	119.00	29.520	29.750	0.30817	1.1094
Tungsten	W...	182.60	184.00	91.300	92.000	0.95300	3.4308
Zinc	Zn...	64.90	65.40	32.450	32.700	0.33873	1.2194
Zirconium	Zr...	89.90	90.60	22.475	22.650	0.23460	0.8445

### Experimental Proof of Faraday's Laws.

Take four beakers and place in them respectively a 10 per cent. solution of copper sulphate slightly acidified with sulphuric acid, a solution of cuprous chloride in hydrochloric acid, a 10 per cent. solution of nickel sulphate, and a solution of cadmium sulphate, with a few drops of sulphuric acid (see p. 282).

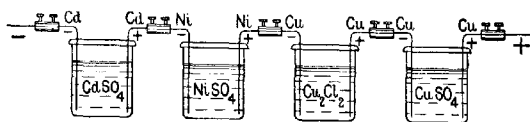


FIG. 1.

Place the beakers in a row close together, and connect them together in the manner shown in Fig. 1. The electrodes marked with the - sign are to be carefully weighed; for the rest, the arrangement of the apparatus explains itself. The anodes and cathodes may be made of sheet metal or of metal rods to which pieces of copper wire have been soldered, in order to connect them together. Electrolytic cells arranged as here shown are said to be connected up in *series*.

Also place in series with the cells an ammeter, so that the intensity of the current may be noted, the strength of the current can be regulated by means of a resistance. Fig. 2 shows diagrammatically the arrangement of the battery, etc. B is the battery or source of current, A the ammeter, C the cells, and R the resistance.

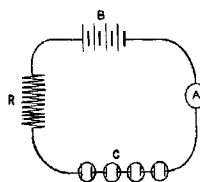


FIG. 2.

In carrying out the experiment, carefully weigh the cathodes, then regulate the current by means of the resistance to, say, 0.5 ampere, and note the time. After allowing the current to pass for one hour, taking care that its intensity remains constant, it is switched off. The cathodes are taken out, washed with distilled water and alcohol, dried in the steam oven and weighed. If the

experiment has been carefully performed, it will be found that the metals have increased in weight in the ratio of their hydrogen equivalents. The current passed should not exceed 1 ampere per square decimeter of cathode surface, otherwise unsatisfactory and badly adhering deposits may be obtained, which are difficult to weigh. It is not by any means an easy matter to obtain satisfactory results from cuprous solutions, as there is a tendency for the deposit to be powdery and not to adhere well. Of course, solutions of other metallic salts may be used instead of those here described.

From what has been already stated, it follows that there is a definite relationship between the valency of an element and the electric charge which the ions carry. Thus the quantity of electricity necessary to deposit 63.6 gm. of copper from a cuprous solution is 96,540 coulombs, but double that quantity is required to deposit the same weight of the divalent copper from a cupric solution. Aluminium, which is trivalent, must have three times the above quantity of current in order to deposit 27 gm. of the metal. 96,540 coulombs of electricity will deposit 200 gm. of mercury from a solution of a mercurous salt, but it requires twice that quantity of electricity to deposit 200 gm. of mercury from a mercuric salt. The same rule applies to the substances liberated at the anode—the current which will liberate 1 gm. of hydrogen will liberate 8 gm. of oxygen, and so on. It must be clearly understood that 96,540 coulombs of electricity deposit the *gram equivalent weight*, and not the gram atomic weight. For example, the gram atomic weight of oxygen is 16, but as oxygen is divalent, the gram equivalent weight is 8. On the other hand, the gram atomic weight of silver is 107.93, but as silver is monovalent, the gram equivalent weight is also 107.93.

## CHAPTER II.

### *MEASUREMENT OF CURRENT.*

THERE are instruments for measuring the intensity or rate of flow of current in a circuit at any given time, and instruments to measure the quantity of current which has passed. Apparatus for measuring quantity of current will first be described. These generally depend upon the amount of gas which is evolved when an aqueous acid or alkaline solution is electrolysed for a given time, or upon the quantity of metal which is deposited from a given metallic solution. By Faraday's Law, we know that a given current will deposit a given weight of copper in a given interval of time, and that, during the same time, the same current will liberate an equivalent quantity of oxygen and of hydrogen from an acidified solution of water.

The apparatus employed for thus determining the quantity of current which has passed in a given time is generally called a **voltameter**. Seeing, however, that we have also instruments called voltmeters for measuring electrical potential, and bearing in mind that the instrument called a voltameter has absolutely nothing to do with volts, but registers the number of coulombs of electricity which have flowed through a circuit, entirely independent of the potential, we propose to call the instrument a **coulometer**. The term voltameter was originally employed to honour Volta, but as his name is perpetuated in the volt, it will be doing no dishonour to him to drop the term voltameter—which is often, especially with beginners, confused with the voltmeter—and substitute the more correct term coulommeter.

### The Coulometer.

**Gas Coulometer.**—There are many forms of coulometer employed for measuring the quantity of electricity which has passed through a circuit in a given time. One of the oldest and best known is the oxygen and hydrogen coulometer, in which the volume of oxygen and hydrogen liberated in a given time is

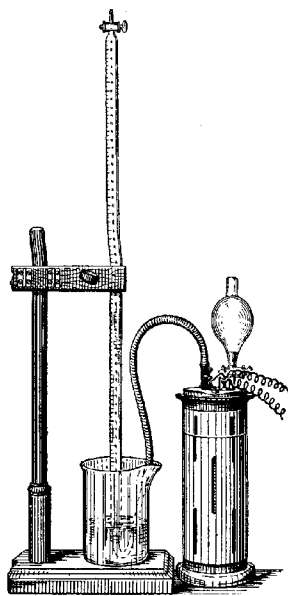


FIG. 3.

measured. There are two forms of this instrument—the **detonating** gas apparatus, in which the two gases are collected together; and the one in which they are collected separately. Fig. 3 shows a detonating gas coulometer. It consists of two cylinders of sheet nickel, placed the one within the other, in a glass cylinder, the



distance between the sheets being about 1 cm. The glass cylinder is closed with a rubber stopper, through which passes a short tube to lead off the liberated gas. A piece of stout nickel wire is riveted on to each of the nickel sheets; these wires are connected to a terminal fastened on the outside of the rubber stopper. The cylinder is nearly filled with a 15 per cent. solution of caustic

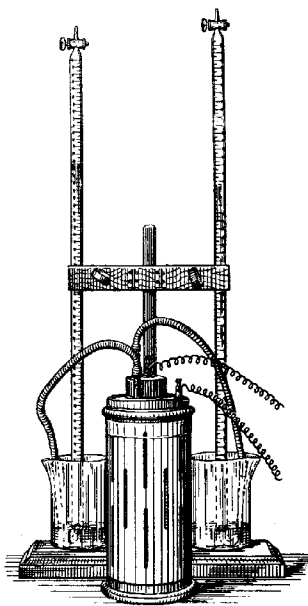


FIG. 4.

soda, which should be free from chlorides. There is also a tap funnel passing through the cork, which is used for filling in distilled water, as it is decomposed by electrolysis. A piece of stout rubber tube is fastened over the outlet tube, by means of which the issuing gas can be collected in a burette or other measuring vessel. When in use the two terminals are connected

with the opposite poles of the source of current. A current of 1 ampere passed for 1 minute liberates 10.45 c.c. of explosive gas, measured at 0° and 760 mm. pressure. In Fig. 4 a similar coulometer for collecting the oxygen and hydrogen separately is shown. In it the nickel anode is separated from the cathode by means of a porous cell. The electrolyte, as in the previous case, is 15 per cent. caustic soda.

As arranged in Figs. 3 and 4, the quantity of gas which can be collected is limited by the size of the burette or measuring cylinder, and therefore the current can only be passed for a short time. The following arrangement, Fig. 5, may be employed

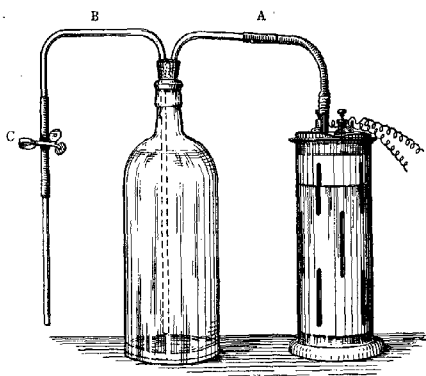


FIG. 5.

when it is desired to pass the current for some considerable length of time. The tube conducting the gas from the electrolyzing cell is connected to a tube, A, passing through a rubber stopper into a large bottle, *e.g.* a Winchester quart. The rubber stopper has a second hole, through which passes a tube, B, bent at right angles, and to which is connected a piece of rubber tubing which can be closed by means of a clip, C. This tube passes to the bottom of the bottle and acts as a siphon. Before commencing an experiment, the bottle is filled with water, the siphon being

also filled, but prevented from running by the clip c. The outer end of the siphon is placed in an empty cylinder. Before the electrolysis is started the clip is opened, when some water will siphon over; but if the apparatus be air-tight it will at once cease running. This water should not be thrown away; on adjusting the levels of the water at the end of the experiment,

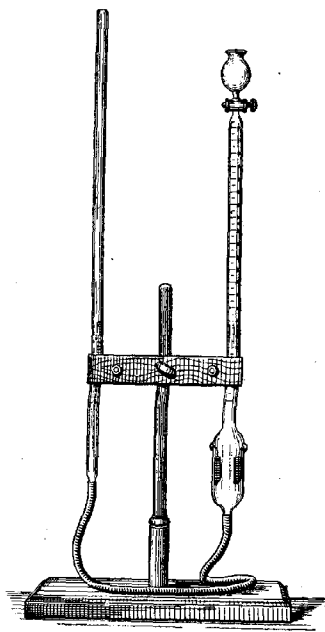


FIG. 6.

it will flow back to the gas reservoir. If, however, the water continues to flow, this will be due to the apparatus not being air-tight, and this must be remedied before proceeding with the experiment.

The electrolysis is now started. From the construction of the apparatus it follows that for every cubic centimeter of gas evolved

1 c.c. of water will pass over into the cylinder. At the end of the operation the levels are adjusted, the clip closed, and the water poured into a measuring vessel. The volume of the gas is then reduced to normal temperature and pressure. In 1 hour 626.4 c.c. of mixed hydrogen and oxygen is evolved at N.T.P., when a current of 1 ampere passes through the coulometer, or 208.8 c.c. of oxygen and 417.6 c.c. of hydrogen. By employing two siphons the oxygen and hydrogen can be collected separately, the coulometer shown in Fig. 4 being then employed.

Coulometers with platinum electrodes containing as electrolyte sulphuric or phosphoric acid are sometimes used. Generally speaking, they have a higher resistance, and the quantity of gas given off is slightly less than should theoretically be obtained, owing to the fact that part of the oxygen is given off as ozone. Neumann's explosion gas coulometer is shown in Fig. 6.

**Weight Coulometer.**—For very exact measurements the silver coulometer is generally employed, because there are very few possibilities of complication occurring in the deposition of silver from its solutions. But this coulometer can only be employed when extremely small currents are being used, because the silver has a tendency to be deposited in a feathery and non-adherent form. Even with low currents silver is obtained as a crystalline deposit from slightly acid or neutral solutions of silver nitrate, such solutions being generally employed in the silver coulometer. The usual form of apparatus employed is shown in Fig. 7. It consists of a

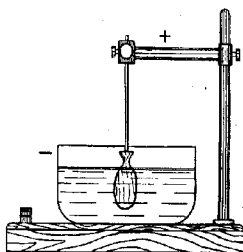


FIG. 7.

weighed platinum or silver basin which serves as cathode and is partially filled with a 7 per cent. solution of silver nitrate. The anode of stout silver rod hangs in the upper portion of the solution, and is wrapped in a piece of thin calico to prevent the silver—which always becomes more or less

disintegrated—from falling into the platinum basin. The calico should be carefully washed in hot water and then rinsed out in distilled water before being used. If it is desired to use a silver coulometer when high currents are being employed, the coulometer must be used on a *shunt* circuit (p. 24), through which only, say, 100th or 1000th of the current is allowed to pass. Or else it should only be kept in the circuit for a very short time, otherwise the amount of silver dissolved from the anode is considerable.

**Copper Coulometer.**—For general work the copper coulometer is the most satisfactory. It is not quite so accurate

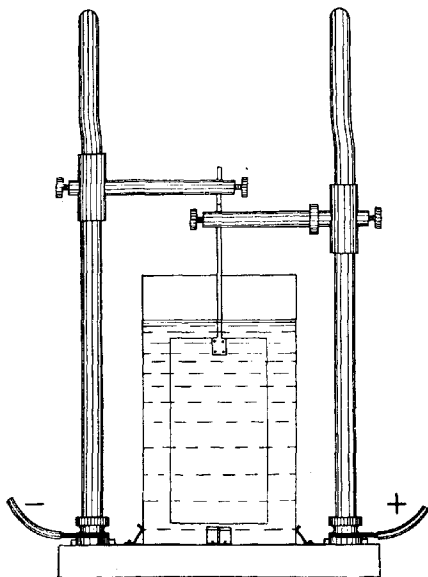


FIG. 8.

as the silver instrument, but is generally quite exact enough for ordinary work, where it is not, as a rule, necessary to know to more than

about 0.25 of an ampere hour how much current has passed. Say, for example, that an operation required the passage of 20 ampere hours, a quarter of an ampere one way or the other would not be of any material importance. Fig. 8 shows a copper coulometer. The cathode hangs in the centre of two anodes, so that an even current density is obtained on either side; in the diagram only one electrode is seen. For preparation of solution see p. 282. In order to obtain a good deposit, and one which adheres firmly, it is not admissible to allow more than 1.25 amperes per square decimeter to pass through the apparatus. Where fairly high currents are being employed, a coulometer of several cells may

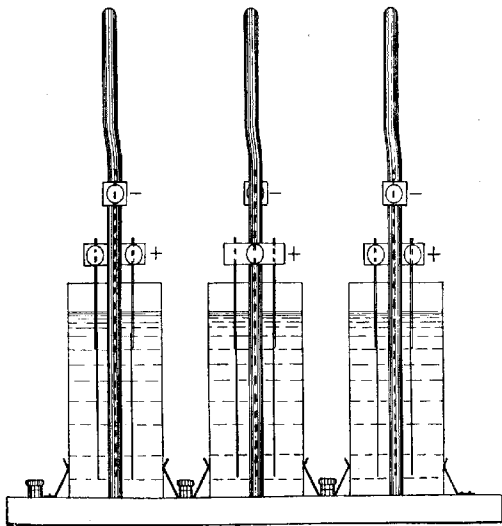


FIG. 9.

be employed. Fig. 9 shows one consisting of three cells, the anodes and cathodes being connected up in parallel (p. 49); by this means three times the anode and cathode surface can be obtained, and therefore three times the current strength be employed as with a single cell of similar size. If a rapid current

of air or carbonic acid gas is passed through the coulommeter, or if the cathode is cylindrical and is rotated, then a very much higher current density can be employed per unit of surface.

The coulommeter, although often indispensable, is at best a tiresome instrument to use, because it is necessary to dry and weigh the cathode plates. This is especially unpleasant when a more or less irregular current is passing, because, in order to know exactly the quantity of current which has passed, it is constantly necessary to stop the current, take out the coulommeter cathodes, dry and weigh them. In order to avoid this

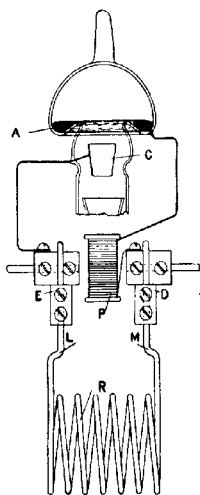


FIG. 10.

difficulty, the Reason Manufacturing Company of Brighton<sup>1</sup> manufacture a mercury coulommeter (Wright's electrolytic metre) in which the mercury, as it is deposited on the cathode, falls into a graduated glass tube. Each gradation in most of the instruments made (the coulommeters are generally made for electric light purposes) represents 1 Board of Trade unit (p. 29), but they can also be made to read in ampere hours. It is not possible to pass a heavy current through a solution of a mercury salt (in this apparatus mercurous nitrate) without the surface of the mercury becoming coated with crystals of mercurous salt. Therefore these instruments are fitted

with a shunt, so that only a definite fraction of the current passes through the mercury solution.

Fig. 10 illustrates the construction and working of the meter.

The current enters at the terminal D, and the greater part of it passes round the low resistance R to the terminal E. The shunt current, which works the coulommeter, and which is always

<sup>1</sup> *Proc. Inst. Elect. Eng.*, 1901, 31, p. 153.

an exact fraction of the total current, passes from D through the fine wire resistance P to the mercury anode A. Thence it goes through the electrolyte to the cathode C, and finally to the terminal E. The relations of P and R are calculated in the first instance, but the exact final adjustment is made by sliding the two wires L and M up or down in two holes drilled in E and D, thus varying the value of R.

When a current is passing through the meter, metallic mercury is deposited on the cathode, whence it falls in minute globules into the first graduated tube G, which reads (Fig. 11) direct in units. This is made in the form of a siphon, so that when it is filled by a quantity of mercury equal to 100 units, it automatically empties itself into the lower tube, which is provided with a scale, S, each division of which is equal to 100 units. The mercury as it is dissolved from the anode is simultaneously replaced by fresh metal drawn from the anode feeder F. This ingenious arrangement acts in the same manner as the well-known "bird-fountain" in keeping the level of the mercury constant.

After the number of units for which the coulommeter was designed have been registered, the meter must be reset to zero. This is done by the simple operation of tilting the whole tube about the hinged supporting brackets, so that all the mercury is returned to the anode feeder.

Fig. 12 shows a complete coulommeter designed to read up to 250 Board of Trade units; this has not the lower scale depicted in Fig. 11. For electro-chemical purposes it is more convenient to have the instrument graduated to read in ampere hours; and, for convenience of moving about, it may be fixed on to a stand.

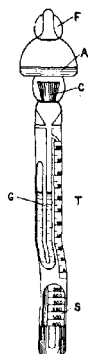


FIG. 11.

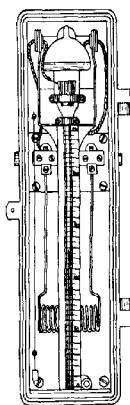


FIG. 12.



## CHAPTER III.

### *INSTRUMENTS FOR MEASURING INTENSITY AND POTENTIAL OF CURRENT.*

#### **Ammeters.**

WHEN a current passes through a wire spiral, a magnetic field is produced, which has the power of attracting a bar of soft iron. Measuring instruments called **ammeters** are made, based upon this property. (A spiral of wire through which the current passes is called a **solenoid**.) It is not within the scope of this book to describe the mechanism of the ammeter; suffice it to say, the ammeter is an instrument which depends upon the property of a spiral of wire to become magnetic when the electric current flows through it. The intensity of the magnetic field is proportional to the amount of current which passes.

Ammeters are arbitrarily graduated, the best instruments being extremely accurate. Fig. 13 illustrates an ammeter made by Messrs. Nalder Brothers & Thompson of London, reading from 0 to 50 amperes. These instruments can also be obtained having a range of 2 amperes, graduated in hundredths of an ampere; and by means of a shunt, the range can be made to extend from 0 to 20 amperes in tenths. For analytical purposes it is very rarely that currents above 2 amperes are required, therefore the lower range of readings can be employed for this purpose, so that instruments made on this shunt system are especially useful for reading very low currents. Such an ammeter must be connected with a two-way switch, the higher or lower reading being obtained by simply changing the direction of the switch.

*Instruments for measuring Intensity of Current.* 23

The Weston instruments are also extremely good, and are very largely used. The case of the Nalder instrument is of brass ;

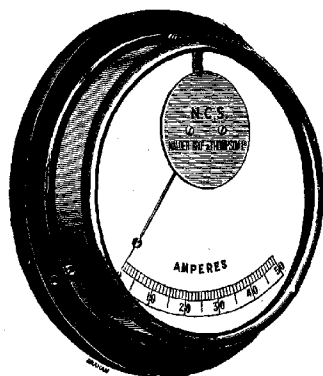


FIG. 13.

the Weston ammeter has usually an iron case, which guards it against outside magnetic influences. Nalder instruments can, however, be obtained with iron cases. Fig. 14 shows a Weston standard portable milliammeter, which is of extreme accuracy, and is often employed for calibrating other instruments. In many instruments, such as the Weston and Nalder ammeters, the whole of the main current does not pass through the instrument, but each

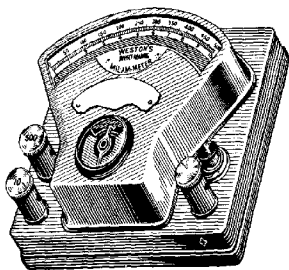


FIG. 14.

instrument is provided with a resistance called a **shunt** ; in other words, the ammeter is placed in a shunt circuit (p. 24). The amount of current which passes through the instrument thus

depends upon the difference of potential between the two ends of the shunt. When the instruments are for taking small currents, the shunt is generally fitted inside the case of the ammeter, but on large station ammeters the shunt is fixed outside the instrument.

## INSTRUMENTS FOR MEASURING POTENTIAL.

### Voltmeters.

An ammeter is an instrument of very low internal resistance; it can therefore be placed in the main circuit, its resistance being so low that it may, for most purposes, be neglected. A voltmeter is practically an ammeter, the coil of which is wound with a large number of turns of very thin wire, and has therefore a very high resistance of several hundreds or thousands of ohms. A voltmeter is therefore always used on a shunt circuit; since, if it were placed in the main circuit, it would oppose so much resistance to the passage of the current, that practically no current would pass, and the instrument would probably be burnt out.

**Shunt Circuit.**—If part of a circuit branches, as shown in Fig. 15, the current has a choice of two paths, A and B. When

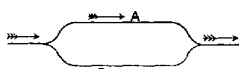


FIG. 15.

the two wires are of equal resistance, then  $\frac{1}{2}$  of the current flows along each wire. But suppose the resistance of A to be 1 ohm,

and that of B to be 10 ohms., then only  $\frac{1}{10}$  of the current will pass along B, the remaining  $\frac{9}{10}$  passing through A.

Now, a voltmeter is of such high resistance that the amount of current which passes through it is inappreciable; in fact, the higher the resistance of the instrument the better, otherwise an appreciable quantity of the current would take this path. Fig. 16 shows the method in which a voltmeter is connected up. The bulk of the

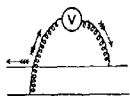


FIG. 16.

current passes along the main conductors, and only a minute fraction of the current passes through the **shunt** circuit. If the

total resistance of the main circuit is 2 ohms, and the resistance of the voltmeter 1000 ohms, then  $\frac{1}{500}$  of the current will pass through the shunt circuit.

An ammeter is often kept in the circuit during the whole time the current is passing; it is not so usual to keep the voltmeter in circuit, because there is a tendency for the instrument to heat, and this, of course, affects its accuracy. Fig. 17 shows a voltmeter; the instrument has a double read-

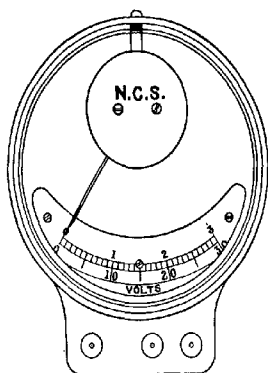


FIG. 17.

ing, on the low side reading from 0 to 3 volts in tenths, and on the high reading from 0 to 30 in half volts.

### Employment of Voltmeter to Measure Current.

Voltmeters can be used to measure current intensity as well as to measure electrical potential. According to Ohm's Law (p. 71), if we know the resistance  $R$  and the potential  $E$  of a circuit, we can calculate the current flowing through it by the equation—

$$C = \frac{E}{R}$$

All that it is necessary to do is to shunt into the main circuit a known resistance. If, for example, a resistance of  $\frac{1}{10}$  ohm is shunted into the circuit, then every volt registered on the instrument represents a reading of 10 amperes, and a reading of  $\frac{1}{10}$  of a volt represents 1 ampere.

$$C = \frac{I}{\frac{1}{10}}$$

With a resistance of  $\frac{1}{100}$  of an ohm, a reading of 1 volt represents 100 amperes. Whereas if the resistance employed is 1 ohm, every volt represents 1 ampere. The employment of a voltmeter for reading current in this way is often very useful in measuring heavy currents. The arrangement of the circuit is represented in Fig. 18. *v* is the voltmeter, which is connected on either side of

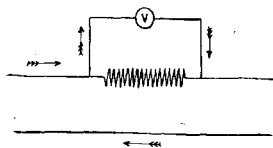


FIG. 18.

the known resistance. Of course, in this method a resistance is placed in the main circuit, but as only very low resistances are employed, this is a matter of very little importance. This method is simply the principle adopted in the Weston and other ammeters, only in these instruments the resistance is usually enclosed in the case of the instrument.

## CHAPTER IV.

### ENERGY.

So far we have dealt only with the measurements of quantity of electricity, and of electrical potential separately. But the energy given out by a dynamo or battery, or used up in an electrolytic process, is not shown by merely reading the current on an ammeter, or the volts registered on a voltmeter—electrical energy is the product of the current and potential.

*An ampere may be defined as the rate of flow of electricity through any cross section of a conductor when there is a difference of potential in the circuit of 1 volt, and the resistance is 1 ohm. Or, more generally, an ampere is the rate of flow of electricity through a conductor when the ratio between the potential and the resistance is one.*

A coulomb, as has been already stated (p. 7), is the quantity of electricity which passes through a circuit in 1 second, when the current intensity is 1 ampere. The unit of electrical energy taken is therefore the **volt-coulomb**.

There is a tendency, on the part of beginners, to look upon the ampere as being a **quantity** of electricity: this is a mistake; the coulomb is a quantity, and is the amount of electricity which passes through a circuit in 1 second, when the current intensity or rate of the flow of the current is 1 ampere. An ampere is no more a quantity than rate of flow of water is a quantity. We may say that if water continue to flow through a pipe of certain cross section at the speed of 1 metre per second in a given time, 10 litres (which is a quantity) of water will have passed a certain point. If the pressure, which governs the rate of flow of the water, is increased, as registered on a pressure gauge, then the

rate of flow of the water will be increased, and therefore a larger volume will pass in a given time. In a similar manner, if the voltage of a current is increased, the current will flow more rapidly, and therefore the ammeter measuring rate of flow will show a higher reading. The voltmeter may therefore be compared to a pressure gauge, and the ammeter to an instrument for measuring speed of flow of a liquid.

The quantity of water which will flow in a given time may also be increased by keeping the pressure constant, but increasing the cross section of the pipe through which it is flowing, *i.e.* decreasing the resistance. In a similar way we can increase the flow of electricity through a circuit by decreasing the resistance, the voltage remaining constant.

It has been found experimentally, by careful measurement in a calorimeter, that, when a coulomb of electricity passes through a circuit in which the drop in potential is 1 volt, 0.2394 calorie is generated.<sup>1</sup> This number we may call the **electrical equivalent of heat**, and it follows that 4.175 volt-coulombs will generate 1 cal. It has also been proved experimentally, that when 1 gm. falls through a space of 42,350 centimeters, it may be made by friction to generate the calorie of heat, *i.e.* to generate enough heat to raise 1 gm. of water from 0° to 1° C. This number is called the **mechanical equivalent of heat**. From the above numbers we find that 1 volt-coulomb expressed in terms of the mechanical equivalent of heat = 10144 gm. cm. (gravitation units).

In referring to work done, or to the energy capacity of a dynamo or other electrical machine, the electrical unit chosen is the volt-ampere-second; this unit is called the **watt**. This is equivalent to saying that 1 coulomb passes in 1 second at a pressure of 1 volt. The watt itself is not often employed, because it is such an extremely small quantity of electricity. The **kilo-watt**, which is 1000 watts, is the unit most generally adopted. From the kilowatt the horse-power can be calculated. In English

<sup>1</sup> In round numbers, this may be taken as 0.24 cal. In other words, when 0.2394 calorie is converted into electrical energy 1 coulomb of electricity is generated.

weights a horse-power is defined as the amount of work necessary to raise 33,000 lbs. through the space of 1 foot in 1 minute. Expressed in metric units, a horse-power is the amount of work expended in raising 75 kilograms through the space of 1 meter in 1 second. Now, a watt is equal to  $\frac{1}{9.81}$  second-kilogram-meters, therefore 1 kilowatt is one thousand times this, or—

$$1000 \times \frac{1}{9.81} = 101.93 \text{ kilogram-meters}$$

But as 1 horse-power is 75 kilogram-meters, it follows that 1 kilowatt is equal to 1.36 horse-power.

$$1 \text{ kw.} = \frac{101.93}{75} = 1.36 \text{ H.P.}$$

**Board of Trade Unit.**—The electrical unit for power and lighting purposes used in this country is called the **Board of Trade unit**, and is the kilowatt hour, which is equal to 1000 volt-ampere hours. Thus if a current of 10 amperes be maintained at a potential difference of 50 volts, in a circuit for 2 hours, then 1 kilowatt of energy will have been used up.

### Calculation of Decomposition Voltage from Thermo-chemical Data.

When two elements combine together, the energy involved in the change makes itself evident in the form of heat. Now, according to the law of the conservation of energy, if a given amount of energy is required to bring about a chemical change, the chemical reaction can only be reversed by application of the same amount of energy again. In order to bring about a reversal of the change, it is not, however, necessary for the energy to be applied in the same form as that originally used. Thus, for example, most chemical changes take place through the addition or absorption of heat; these changes can be reversed by the application of an equivalent addition of electrical energy. If, therefore, we know the heat of combination of a substance, it



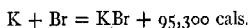
is easy to calculate the voltage which is necessary to decompose or electrolyse the substance. For example, the heat of combination of sodium and chlorine is 97,300 calories. On p. 28 we found that one volt-coulomb of electricity generates 0.24 calorie, therefore the number of volt-coulombs which corresponds to 97,300 calories is—

$$\frac{97,300}{0.24} = 405,417 \text{ volt-coulombs}$$

Now, according to "Faraday's Law" (p. 7), 96,540 coulombs of electricity, *i.e.* one faraday, is necessary to decompose the gram-molecule of a substance. If, therefore, we divide this into the number just obtained, we obtain the decomposition voltage of sodium chloride as—

$$\frac{405,417}{96,540} = 4.182 \text{ volts}$$

Or take the case of potassium bromide—



From this we obtain the number of volt-coulombs corresponding to the calories, as—

$$\frac{95,300}{0.24} = 397,083 \text{ volt-coulombs}$$

and the decomposition voltage as—

$$\frac{397,083}{96,540} = 3.193 \text{ volts}$$

As a further example, zinc chloride may be taken; the thermo-chemical equation is—



The volt-coulombs requisite are, therefore—

$$\frac{97,200}{0.24} = 405,000 \text{ volt-coulombs}$$

and the decomposition voltage—

$$\frac{405,000}{96,540} = 4.099 \text{ volts}$$

The decomposition voltages here given must be employed in order to decompose the several substances. But it will generally be found necessary in actual practice to employ slightly higher voltages, owing to the resistance of the bath, the distance of the electrodes apart, and other mechanical causes which invariably arise.

The electrolysis of aqueous solutions is slightly different. Here we are dealing with substances which are ionised, and these ions carry the current; the mere fact of the passage of the current, therefore, takes place without expenditure of energy. Work is only done at the electrode when the electrical charge is neutralised, and the work done is in neutralising the polarisation current, which exerts an electro-motive force in the reverse direction to the primary current which is being passed. Le Blanc<sup>1</sup> found that with platinum electrodes the electromotive force of polarisation is independent of the nature of the electrolyte, when the substance which separates at the electrode is the same. Thus the values for *E* with all oxygen acids and bases is the same, viz. about 1.70 volts.

Certain differences, however, are noticed with acids in which the products of electrolysis are not the same. For example, with the halogen acids the tensions obtained for normal solutions are—

	Volts.
HCl . . . . .	1.31
HBr . . . . .	0.94
HI . . . . .	0.52

The reason that these acids show a lower value for *E* is traceable to the simultaneous separation of hydrogen and oxygen at the electrodes, along with the halogen. As the dilution of hydrochloric acid increases, more and more oxygen is liberated in comparison with the halogen, and consequently the polarisation tension, *i.e.* the value of *E*, rises, so that at  $\frac{N}{22}$  solution the value for *E* is 1.69.

Appended is a table of some of the best-known acids and bases with the values for *E*, which have been experimentally found.

<sup>1</sup> *Zeit. Phys. Chem.*, 1891, 8. p. 299; 1892, 12. p. 333.

TABLE II.

ACIDS.		Volts.
Sulphuric acid . . . . .		1'67
Nitric acid . . . . .		1'69
Hydrochloric acid $\frac{N}{22}$ . . . . .		1'69
Phosphoric acid . . . . .		1'70
Monochloroacetic acid . . . . .		1'72
Dichloroacetic acid . . . . .		1'66
Malonic acid . . . . .		1'69
Perchloric acid . . . . .		1'65
BASES.		Volts.
Sodium hydrate . . . . .		1'69
Potassium hydrate . . . . .		1'67
Ammonium hydrate . . . . .		1'74
Methylamine $\frac{N}{4}$ . . . . .		1'75
Diethylamine $\frac{N}{2}$ . . . . .		1'68

The decomposition values of the salts of various metals are different for each metal. But the values for sulphates and nitrates of the same metal are very nearly equal. The decomposition values for the salts of the strongly ionised acids have nearly the same value—viz. about 2'20 volts.

TABLE III.

	Volts.
Sodium nitrate . . . . .	2'15
Potassium nitrate . . . . .	2'17
Strontium nitrate . . . . .	2'28
Calcium nitrate . . . . .	2'11
Barium nitrate . . . . .	2'25
Sodium sulphate . . . . .	2'21
Potassium sulphate . . . . .	2'20

With the halogen acids the numbers are slightly lower.

TABLE IV.

	Volts.
Sodium chloride . . . . .	1'98
Potassium chloride . . . . .	1'96
Lithium chloride . . . . .	1'86
Calcium chloride . . . . .	1'89
Strontium chloride . . . . .	2'01
Sodium bromide . . . . .	1'58
Potassium bromide . . . . .	1'61
Sodium iodide . . . . .	1'12
Potassium iodide . . . . .	1'14

The next table shows the decomposition voltage of a few substances in which the metal is deposited at the cathode.

TABLE V.

	Volts.
Zinc sulphate . . . . .	2.35
Zinc bromide . . . . .	1.80
Nickel sulphate . . . . .	2.09
Nickel chloride . . . . .	1.85
Lead nitrate . . . . .	1.52
Silver nitrate . . . . .	0.70
Cadmium sulphate . . . . .	2.03
Cadmium nitrate . . . . .	1.98
Cadmium chloride . . . . .	1.88
Cobalt sulphate . . . . .	1.92
Cobalt chloride . . . . .	1.78

It will be noticed that salts of the same metal with different acids give slightly different decomposition voltages. This fact may be made use of in separating the metals from each other by gradation of potential, although its application is very limited. For further information on the subject the student should study the original literature or text-books upon the physical side of electro-chemistry. For example, that of Le Blanc, Arrhenius, Leffeldt, H. Jones, or the works of Ostwald.

## CHAPTER V.

### *SOURCES OF CURRENT.*

THERE are practically only two sources from which current is obtained for electro-chemical work, the dynamo and secondary batteries or accumulators. The use of primary cells, except in cases where only a small and intermittent current is required, has been almost discontinued, partly because of the trouble required to charge and recharge them, and also because of their inconstancy. Considering the inconvenience of primary cells, one is really astonished at the amount of important pioneering work in connection with electro-chemistry which Davy, Bunsen, and others carried out with their aid. As, however, a knowledge of the theory of the primary battery is of great use in understanding the mechanism of the secondary battery, and because for certain purposes they are still of great practical importance, a few of the principal cells will be described here.

### **Introduction.**

If a piece of zinc is placed into a solution of copper sulphate, the zinc gradually goes into solution as zinc sulphate, and copper is deposited out. We have here a chemical change taking place, and the progress of the change is accompanied by the evolution of heat.

Now, suppose that a rod of zinc is placed in a porous cell filled with zinc sulphate solution, and this porous cell is put into a beaker containing a solution of copper sulphate in which is also placed a rod of copper. It is obvious that neither the zinc nor

the copper will pass into solution. But connect the zinc to the copper by means of a piece of wire, and it is found that the zinc commences to dissolve, and that for every equivalent of zinc which passes into solution an equivalent of copper is plated out upon the copper rod. But this is not all; if now a galvanometer is brought near to the wire which connects the zinc to the copper, the needle of the galvanometer becomes deflected—showing that there is an electric current flowing through the wire.

Here we have chemical energy being transformed into electrical energy. In the first example, in which zinc was placed into a solution of copper sulphate, the chemical energy made itself manifest in the form of heat. In the second case the chemical energy is transformed into electrical energy.

Now, because the zinc passes into solution and the copper becomes deposited out, we say that the current passes in the outer circuit, *i. e.* through the connecting wire, from the copper to the zinc, and through the solution from the zinc to the copper. The zinc is therefore called the **negative pole** and the copper the **positive pole**, but the zinc is said to be electro-positive to the copper. The plate which goes into solution and is electro-positive to the other metal forms the negative pole in the external circuit. Thus one often refers to the zinc or negative pole, because the zinc is electro-positive to the other metals.

### Positive and Negative, Relative Terms.

It must, however, be distinctly understood that the terms positive and negative are purely relative. By changing the conditions we can cause the metal which before was negative to become positive. A very good example of this is found in a cell in which the opposite plates are copper and aluminium, both metals being in the same electrolyte.

1. In the first place, caustic soda is employed as the electrolyte, the aluminium will go into solution, but the copper will not: the aluminium is therefore electro-positive to the copper, and the current passes in the external circuit from the copper

to the aluminium, in the solution from the aluminium to the copper.

2. Secondly, use nitric acid as the electrolyte; the copper will now go into solution, but the nitric acid has practically no action upon the aluminium, therefore now the aluminium is electro-negative to the copper, and the current passes in the external circuit from the aluminium to the copper, and through the electrolyte from the copper to the aluminium.

3. Finally, an example might be given of a cell in which the poles are of the same metal, yet one is negative and the other positive. Such a cell can be made with two aluminium plates, separated from each other by means of a porous diaphragm. The one plate immersed in strong nitric acid, and the other in a solution of caustic potash. Under these conditions, the aluminium plate in contact with the caustic potash will pass into solution, but that immersed in the nitric acid will be unacted upon. We therefore have the aluminium plate, which is standing in caustic potash, electro-positive to the plate surrounded with the nitric acid. Consequently the current passes in the outer circuit from the aluminium immersed in nitric acid to the rod standing in the caustic soda.

From these examples it is obvious that the terms negative and positive are relative, and that when we say one metal is electro-negative to another, it must be remembered that under certain conditions the order of sign may be reversed. In fact, it is simply a question of chemical action taking place. If we have two metals, A and B, and a given solution, the question whether A is electro-negative or electro-positive will depend whether A or B is acted upon by the solution. If, for example, A is dissolved by the solution, but B is unacted upon by it, then A will be electro-positive to be B, and *vice versa*. Platinum and carbon are electro-negative to other metals because they are not acted upon by solvents.

In the following table the metals are arranged in their order of sign when placed in various solutions, the most electro-positive being placed at the head of the column. It will be noticed that

in all the solutions zinc is electro-positive to all the other metals; from this it follows that zinc will replace all other metals, itself going into solution and the other metals being precipitated out. The other metals, however, are not always in the same order. Lead, for example, would replace tin from nitric acid solutions, but from solutions in sulphuric acid tin would replace lead. In a solution acidified with sulphuric acid, nickel would replace copper, but from alkaline solutions copper would replace nickel.

TABLE VI.

Dilute nitric acid.	Dilute sulphuric acid.	Ammonium chloride solution.	Sodium chloride solution.	Potassium hydroxide solution.
+ Zinc + Lead + Tin + Iron + Nickel + Bismuth + Antimony + Copper - Silver —	+ Zinc + Iron + Tin + Lead + Aluminium + Nickel + Antimony + Bismuth + Copper - Silver	+ Zinc + Lead + Tin + Iron + Bismuth + Antimony + Silver + Mercury + Carbon - Platinum	+ Zinc + Lead + Tin + Iron + Antimony + Bismuth + Copper + Silver - Platinum —	+ Zinc + Tin + Antimony + Lead + Bismuth + Iron + Copper + Nickel - Silver —

## Potential and Polarisation.

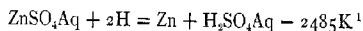
The electro-motive force (E.M.F.) or potential of a cell is dependent upon the heat of solution of the electro-positive metal in the solvent which forms the electrolyte. Theoretically, therefore, the potential of the cell should remain constant until the whole of the metal has gone into solution.

Practically, for several reasons, this is not the case. In the first place, the concentration of the electrolyte is continually varying. As the metal passes into solution, the strength of the electrolyte decreases; therefore solution of the metal is retarded, and, as a consequence, the number of calories given out in a given time is less, and the E.M.F. therefore falls—the cell becomes **polarised**. In the second place, in a great many cells gas is given

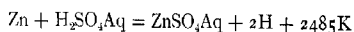


off at the poles when they are in use, and this gas produces gaseous polarisation. An example will serve to make this clearer.

When a plate of zinc and a plate of copper are immersed together in a beaker of dilute sulphuric acid, and are connected together by means of a piece of copper wire, an electric current passes through the wire from the copper to the zinc. But after a short time it is found that the current becomes weaker and weaker, and finally may be hardly perceptible. This weakening of the current is due to **polarisation**. In order that a complete cycle may be made by the current, it must not only pass along the wire from the copper to the zinc, but must also pass through the solution from the zinc to the copper. Now, when the electric current passes through the electrolyte, decomposition of the water takes place, and oxygen and hydrogen are liberated. In the case under consideration, the oxygen being liberated at the surface of the zinc, oxidises it to zinc oxide, but this immediately dissolves in the dilute sulphuric acid with formation of zinc sulphate, therefore the surface of the zinc always has a clean metallic appearance. At the same time the hydrogen is yielded up on the surface of the copper; this element, however, is unable to form a compound with the copper, but produces a thin coating of gas upon the surface of the metal. The dilute sulphuric acid is now no longer able to come in direct contact with the copper, and a resistance is thus opposed to the passage of the current; furthermore, we may suppose that there is a tendency for the hydrogen, as it is liberated, to reduce the zinc sulphate with reformation of zinc and sulphuric acid.



This reaction is contrary to the primary reaction which is the solution of the zinc in the sulphuric acid. In other words, the electric current is proportional to the heat produced by the exothermic reaction—



<sup>1</sup> The symbol K represents Ostwald's calorie, which is one hundred times greater than the small calorie (cal.), and ten times less than the large calorie (Cal.). We have thus—

1 Cal. = 10 K. = 1000 cal.

that is, the heat of solution of the zinc in sulphuric acid, but by the reduction of the zinc sulphate to zinc and sulphuric acid we have an endothermic reaction; therefore the one will neutralise the other.

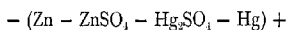
The polarisation effects are said to produce a **back electromotive force**. The back E.M.F., acting in a reverse direction to the primary E.M.F., neutralises part of the primary potential, and thus the voltage of the cell falls. If, for example, the potential of a cell when it is first made up is 1.3 volts, and after a short time, owing to polarisation, a back E.M.F. of 1 volt is set up, then the potential of the cell falls to 0.3 volt, and the current, of course, falls at the same time.

In all primary cells which are in any way satisfactory, **depolarisers** are used to prevent, or, at any rate, retard, polarisation. Either an oxidising agent is used as a depolariser, its function being to oxidise the hydrogen with formation of water; or the positive pole may be placed in a solution from which there is plated out the metal of which the positive pole consists; in this case there is no formation of gas, and the depolariser may be said to be metallic.

Even although depolarisers are employed to keep the cells as constant as possible, no primary cell can be termed constant; therefore they cannot be used as standards of potential.

## Standard Cell.

The cell which is generally used for a standard was devised by Latimer Clark in 1872.<sup>1</sup> It consists of an amalgam of pure zinc and pure mercury, covered with mercurous sulphate and a saturated solution of zinc sulphate.



The form of cell devised by Lord Rayleigh<sup>2</sup> is shown in

<sup>1</sup> *Proc. Roy. Soc.*, xx., 444.

<sup>2</sup> *Phil. Trans. Roy. Soc.*, xvii. 411 (Part II., 1884).

Fig. 19; this cell, known as Lord Rayleigh's H form, is constructed as follows:—

One of the legs is filled to about one-fifth of its height with an amalgam of zinc, A, formed by placing pure zinc into pure mercury which has previously been distilled in vacuum; the other leg with pure mercury, B, and is covered with a layer of mercurous sulphate, C; the whole is then filled up above the level of the

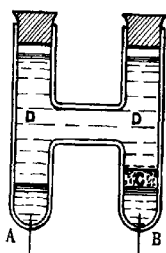


FIG. 19.

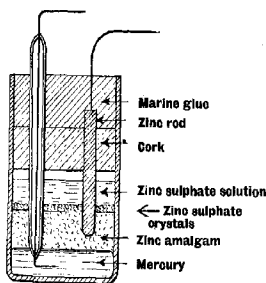
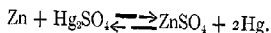


FIG. 20.

cross tube with a pure saturated solution of zinc sulphate, DD, crystals of zinc sulphate being added to ensure the solution always being saturated. The two tubes are then closed by paraffined corks in order to prevent evaporation. Electrical contact is made by means of the two platinum wires fused through the two legs of the H tube.

Fig. 20 shows the Board of Trade form of Clark's cell.

The chemical energy of the Clark cell is represented by the following equation.



When read from left to right, the equation represents the discharge of the cell; when read in the opposite direction the charging of the cell.

The E.M.F. of the Clark cell at 15° is 1.4328 volt.

The constancy of the Clark element is due to having always a

saturated solution of the electrolyte present; there is no possibility of gassing, because the electro-positive metal goes into solution, and the electro-negative metal is deposited out.

There is, however, one source of inconstancy in the Clark cell, and that is the variation of potential produced by changes in temperature. Thus—

At 15° the E.M.F. is 1.4328 volt.

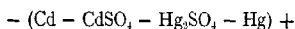
„ 20° „ „ „ 1.4267 „

„ 30° „ „ „ 1.4134 „

The temperature co-efficient for each degree above 15° is 0.0011 volt.

### Weston Cadmium Cell.

The Weston cell in which we have



is made on the same system as the Clark cell, but it has one great advantage over it in having an extremely low temperature coefficient. Fig. 21 shows the cell diagrammatically, as described by Dr. Henderson, without the need of further explanation.

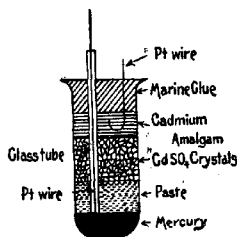
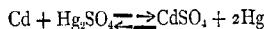


FIG. 21.

The formula representing the chemical energy of the Weston cell is shown in the following equation:—



The E.M.F. of the Weston cell is 1.019 volts, and this is practically the same for all temperatures. The Weston cell is now largely superseding the Clark cell as a standard for measuring potential.

It must be remembered that neither the Clark nor the Weston cell can be employed for obtaining current, the amount of current generated being infinitesimal.

## PRIMARY CELLS.

### The Daniell Cell.

One of the most simple and at the same time efficient of primary batteries is the **Daniell cell**. Fig. 22 shows the cell diagrammatically in its simplest form. It consists of an amalgamated zinc rod in dilute sulphuric acid or a solution of zinc sulphate,

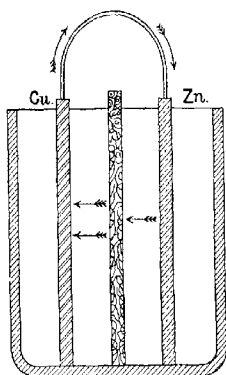
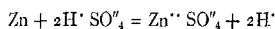


FIG. 22.

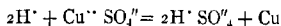
and a copper rod in a saturated solution of copper sulphate. The two solutions are separated from each other by means of a porous partition.

The zinc rod is the negative pole, and the copper rod the positive pole. On connecting the two poles together by means of a piece of wire a current flows through the wire from the copper to the zinc plate, and through the solution from the zinc to the copper plate. When the current passes, owing to the zinc having a greater tendency than the copper to pass into solution and form a compound with the electrolyte, the zinc dissolves and the copper becomes plated out from the copper sulphate solution upon the copper rod or plate. The action may be represented by the following equation :—



The hydrogen is not liberated as gas, but while in the ionic state passes with the current to the copper sulphate solution, where it

interchanges with the Cu of the  $\text{CuSO}_4$  with reformation of sulphuric acid and deposition of non-ionised copper.



It is obvious that after the current has passed for some time all the copper will become plated out, when of course the cell will cease to work. In order to avoid this, in the modern forms of the cell, provision is made for keeping the concentration of the copper sulphate constant. Fig. 23 shows in section the form of cell now generally employed. It consists of a cylindrical copper vessel, A, which acts as the + pole; this is filled with the solution of copper sulphate, and has standing in it a porous earthenware cylinder, B, which contains the dilute sulphuric acid and the zinc rod. Running round the top of the inside of the copper vessel there is a perforated tray of copper; this is kept filled with crystallised copper sulphate, which goes into solution as the copper is deposited from the copper sulphate.

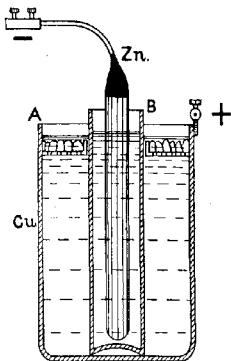
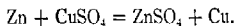


FIG. 23.

In this cell we really have the **non-ionised** zinc exchanging with the ionised  $\text{CuSO}_4$ . That is, the zinc takes on an electric charge, and the copper becomes electrically neutral. The chemical action thus resolves itself into an exchange of ions, and the equation might therefore be written—



The **depolariser** in the Daniell cell is a **metallic** one. In the first place, the zinc cannot polarise, because it goes into solution. There is no polarisation at the copper, because the hydrogen never assumes the non-ionised state, but simply changes place with the

copper of the copper sulphate, which becomes plated upon the copper of the + pole.

The E.M.F. of the Daniell cell varies from 1.178 volts, when 1 part by volume of sulphuric acid to 12 parts by volume of water is employed, to 1.07 when a concentrated solution of zinc sulphate is used.

### Bunsen Cell.

The Bunsen cell, as shown in Fig. 24, consists of a glass vessel nearly filled with dilute sulphuric acid (1 vol. acid, 2 vols. water),

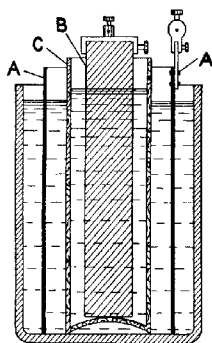


FIG. 24.

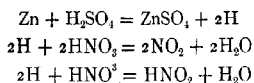
and containing a zinc plate, A, which is amalgamated with mercury to minimise the local action of the sulphuric acid. The zinc plate is bent in the form of a cylinder, and surrounds a porous cell containing concentrated nitric acid; the porous cell C contains the positive pole B, which is made of gas carbon or of graphite.

In preparing this cell, the carbon should be heated, and should then have about an inch of one end dipped in melted paraffin; because

if this is not done, after being used for some time, the nitric acid gradually creeps up the carbon and corrodes the brass binding-screws. The zinc should be well amalgamated by rubbing it with dilute sulphuric acid and mercury; this can be done by means of a stick with a piece of cloth tied on the end. Finally, the porous cell should be soaked for about twenty minutes in dilute sulphuric acid before being used.

In this battery the depolariser is the nitric acid which oxidises the hydrogen. Hence, the longer the cell remains in operation the weaker the nitric acid becomes, from the reducing action of the hydrogen. Therefore its efficiency becomes less, and after the battery has been in use for some time, the current becomes

much weaker. The fuming of the nitric acid owing to the formation of nitrogen peroxide is another great objection to this form of the Bunsen cell. The following equations represent the reactions which take place.



The E.M.F. of the Bunsen cell, when in good working order, is from 1.8 to 1.86 volts.

### Chromic Acid Cell.

The chromic acid cell is really a modification of the Bunsen cell; it contains a solution of sulphuric acid with sodium or potassium dichromate as depolariser. The negative pole is of amalgamated zinc, and the positive pole of retort carbon. The solution employed is the same for both poles, therefore there is no necessity for separating them by means of a porous cell, consequently the internal resistance of the cell is less than that of the one just described. The solution employed may consist of 200 grm. sodium dichromate dissolved in 1 litre of water, to which is then added 150 c.c. of concentrated sulphuric acid. Or, if potassium dichromate is employed, dissolve 105 grms. in 1 litre of water and add 110 c.c. of concentrated sulphuric acid.

The most convenient form of this battery is illustrated in Fig. 25. It consists of a thick glass flask containing the solution; two carbon plates which serve as the positive pole dip into the solution; the negative pole, consisting of an amalgamated zinc plate, is placed between the carbons. When not in use, the zinc plate

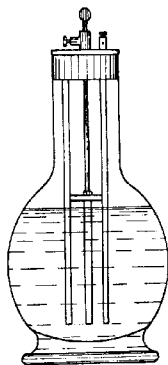
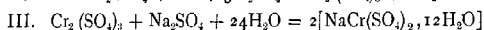
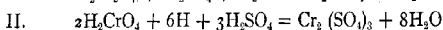
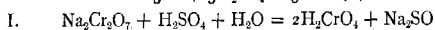
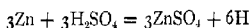


FIG. 25.



can be drawn up, and this prevents its being corroded away. The reaction which takes place may be represented by the following equations :—



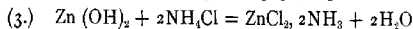
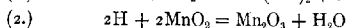
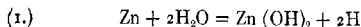
When sodium dichromate is used as shown in the above equations, very little of the sodium chrome alum crystallises out, owing to its solubility, but when potassium dichromate is employed the crystals of potassium chrome alum often cause the carbon plates to disintegrate, when the battery is left out of use for some time. It is also better to use the sodium dichromate for another reason, viz. because weight for weight the sodium salt yields a larger amount of  $\text{CrO}_3$ .

### **Leclanché Cell.**

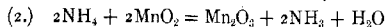
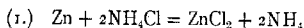
The Leclanché cell is very largely used in telegraphy, and for other purposes, such as electric bells, where the current is only required intermittently. It consists of a negative zinc pole and a positive carbon pole; the electrolyte is ammonium chloride, and the depolariser manganese dioxide.

The carbon pole A, which is made of gas carbon, is placed in a porous cell and surrounded with a mixture of granular manganese dioxide and broken gas carbon. The top of the cell is generally closed in with a coating of pitch, through which passes a glass tube to allow ingress of air and egress of gases. The outer cylinder, which contains the negative pole—a zinc rod, B—is of glass, and contains a concentrated solution of ammonium chloride.

A very usual form of the cell is shown in Fig. 26. The chemical reactions which take place in the cell are perhaps rather complicated, but the equations below probably give a fair idea of what occurs.



When the cell is working there is always a smell of ammonia produced, so that probably the following reaction also takes place—



Probably only a very small portion of the ammonia shown in the last equation will be evolved in the free state, the major portion combining with the zinc chloride to produce the double salt ( $\text{ZnCl}_2 \cdot 2\text{NH}_3$ ).

The E.M.F. of the Leclanché cell lies between 1·4 and 1·6 volts, and is generally, after being in use for some time, about 1·28 to 1·3 volts. The internal resistance of different cells varies widely, in some cases being as low as 0·4 of an ohm, while in others it may be several ohms. When the cell is in constant use, it rapidly loses strength through the reduction of the manganese dioxide and consequent polarisation. But if left for some time unused, it gradually returns to its original condition, owing to the oxidation of the manganese sesquioxide back to manganese dioxide again.

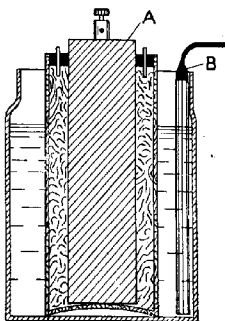
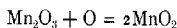


FIG. 26.

### Cupron Element.

The cupron element, or Lalande cell, consists of a positive pole made of a plate of compressed cupric oxide, A, which hangs between two amalgamated zinc plates, B, B, in a solution of caustic

potash or soda, as shown in Figs. 27, 28. The cupric oxide acts as the depolariser, and as soon as this becomes reduced, the cell ceases to act properly. The cupric oxide, being of a porous structure, is readily regenerated. This is done by taking the

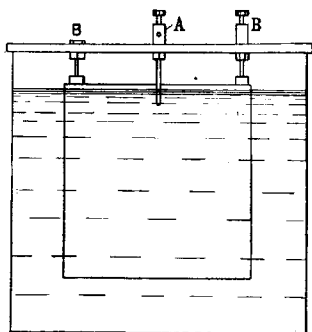


FIG. 27.

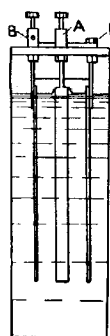
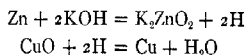


FIG. 28.

positive plate out of the solution, washing it with water, and then exposing it to the air for from 20 to 30 hours. If, however, it is heated to 100 or 180° the oxidation is complete in 30 to 40 minutes. The chemical changes which take place are very simple, and may be expressed as follows :—



When the battery has been in use for some time the electrolyte requires renewing, and the zinc plates, which become coated with a greyish deposit of hydrated sodium zincate, should be scraped and reamalgamated.

One advantage of the cell is its very low internal resistance. The E.M.F., however, is rather low, being at the commencement 1·2 volts. This rapidly falls to 0·82 of a volt, at which point it remains constant until the electrolyte becomes almost exhausted or the copper oxide reduced.

### Grouping of Cells.

For obtaining a high E.M.F., cells should be connected in **series**, for producing a low internal resistance, in **parallel**. Fig. 29 shows three Bunsen cells connected in series, the opposite poles

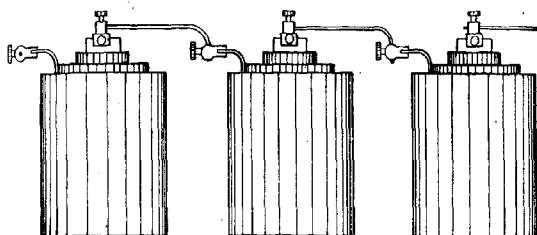


FIG. 29.

of neighbouring cells being connected up together; the zincs, it will be seen, are joined to the carbons. The E.M.F. of such a system is three times that of a single cell; *i.e.* if we take the E.M.F. of a Bunsen cell as 1·8 we get  $1\cdot8 \times 3 = 5\cdot4$  volts.

Connecting the cells up in series, although it increases the E.M.F., also increases the internal resistance of the system.

Fig. 30 represents three Bunsen cells connected in parallel,

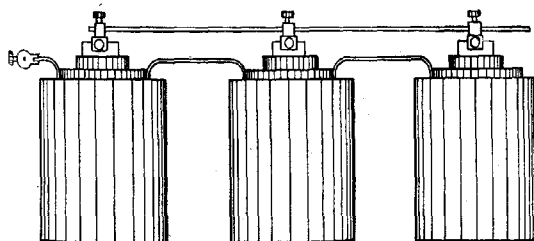


FIG. 30.

the zincs to the zincs and the carbons with the carbons. This arrangement decreases the internal resistance of the cell: the

internal resistance of two cells connected in parallel is only half the resistance of one alone, and of three cells only one-third. The effect of joining up in parallel is really to increase the size of the plates: if a plate has a surface of 100 sq. centimeters, then, connecting it in parallel with another cell of equal size is equivalent to having a plate of 200 sq. centimeters surface.

*When the external resistance is high, cells should be connected in series; but when the external resistance is low, they should be connected in parallel.*

This will be best shown by means of a few examples. Ohm's Law says: "*The current strength in a circuit is equal to the electromotive force divided by the resistance of the circuit, i.e. the internal resistance plus the external resistance.*"

If, then,  $b$  is the internal resistance of the system,  $r$  the external resistance, and  $E$  the electromotive force, then the current strength  $C$  will be represented by the formula—

$$C = \frac{E}{b + r}$$

It follows from this formula that  $C$  may be increased either by increasing the electromotive force,  $E$ , or by decreasing the internal resistance,  $b$ .

#### EXAMPLE I.

The E.M.F. of a cell is 1.1 volts. The internal resistance is 0.8 ohm. The external resistance is 15 ohms. With various groupings we can obtain—

##### A. Connecting in Series.

$$1 \text{ cell} \quad C = \frac{1.1}{0.8 + 15} = 0.069 \text{ amp.}$$

$$2 \text{ cells in series} \quad C = \frac{2 \times 1.1}{2 \times 0.8 + 15} = 0.133 \text{ amp.}$$

$$6 \text{ cells in series} \quad C = \frac{6 \times 1.1}{6 \times 0.8 + 15} = 0.333 \text{ amp.}$$

**B. Connecting in Parallel.**

$$2 \text{ cells in parallel } C = \frac{1.1}{\frac{0.8}{2} + 15} = 0.071 \text{ amp.}$$

$$6 \text{ cells in parallel } C = \frac{1.1}{\frac{0.8}{6} + 15} = 0.072 \text{ amp.}$$

**EXAMPLE II.**

With an external resistance of 0.15 ohm.

**A. Connecting in Series.**

$$1 \text{ cell } C = \frac{1.1}{0.8 + 0.15} = 1.15 \text{ amps.}$$

$$2 \text{ cells in series } C = \frac{2 \times 1.1}{2 \times 0.8 + 0.15} = 1.25 \text{ amps.}$$

$$6 \text{ cells in series } C = \frac{6 \times 1.1}{6 \times 0.8 + 0.15} = 1.33 \text{ amps.}$$

**B Connecting in Parallel.**

$$2 \text{ cells } C = \frac{1.1}{\frac{0.8}{2} + 0.15} = 2.0 \text{ amps.}$$

$$6 \text{ cells } C = \frac{1.1}{\frac{0.8}{6} + 0.15} = 4.11 \text{ amps.}$$

In order to decrease the internal resistance of a battery, and yet maintain a fairly high E.M.F., it is often useful to connect up the cells partly in series and partly in parallel. Fig. 31 represents diagrammatically a set of twelve cells connected in three sets of four cells each. Such a battery will give an electromotive force equal to four cells, but the resistance of the system will be one-third of that which would be exerted by three cells.

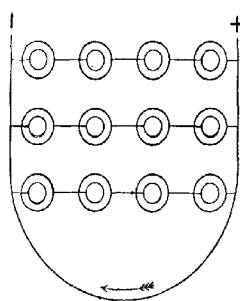


FIG. 31.

after a little experience in determining which, for different work, is the best grouping of his cells, in order to obtain the maximum efficiency from his battery. The rule for grouping is to connect up in such a manner that the internal and external resistance are as nearly as possible the same. Under such conditions, the greatest efficiency is obtained.

### Accumulators.

It has already been shown that in a Daniell cell (p. 42) the electric current passes through the solution from the zinc to the copper, and, in the outer circuit, from the copper to the zinc—the zinc going into solution, and the copper being deposited out. If now a current from a dynamo or other source of electrical energy is caused to pass in the opposite direction—from the zinc to the copper in the outer circuit, and through the solution from the copper to the zinc—the copper will go into solution, and the zinc will be deposited upon the zinc electrode. The battery will thus be regenerated, and if the same amount of current is passed in this, the reverse direction, as was originally taken out of the battery, the cell will have obtained its original condition. In the first place, chemical energy was converted into electrical energy; and in the second, electrical energy has been converted into chemical energy. That is, electrical energy has been stored up in the form of chemical energy, from which it can be again obtained; this is the principle of the **accumulator** or **storage cell**. *The storage cell is a reversible cell, and is an apparatus for storing up electrical energy in the form of chemical energy.* By a reversal of the action this chemical energy can

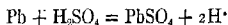
again be converted into electrical energy. For many reasons the Daniell cell does not make a satisfactory accumulator, and it is never so used in practice.

### **The Lead Accumulator.**

The lead accumulator consists of a positive pole of lead peroxide ( $\text{PbO}_2$ ), and a negative pole of spongy lead. The first lead accumulator made was that of Planté in 1860. Planté prepared his cell by passing the electric current through sulphuric acid, in which both the negative and the positive pole were of lead. When the current was passed, the positive lead plate became covered with a brown coating of lead peroxide, while the surface of the negative plate became more or less spongy. On stopping the current and connecting the positive and negative plates together, an electric current was produced. Planté found that this process of charge and discharge could be repeated as often as he liked, and that the more often it was repeated the greater became the capacity of the cell. It is not in the scope of this book to go into details of the various methods of making accumulators, or of the rival merits of the different kinds. It must suffice to say that accumulators at the present day are rarely made by this costly method of charge and discharge, but the active material is generally made in the form of a paste which is caused to adhere to a lead grid.

### **Chemical Process.**

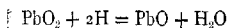
The plates having been properly formed, consist, then, of the positive lead peroxide plate and the negative plate of spongy lead. On discharge, the negative plate becomes converted into lead sulphate—



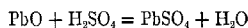
The hydrogen ions convey the positive electricity to the peroxide plates, and there give up their charge. At the moment the



hydrogen yields up its charge it reacts with the lead peroxide, and reduces it to lead monoxide—



This lead monoxide then reacts with the sulphuric acid, and is converted into lead sulphate—



The positive current flows from the lead plate (Fig. 32) through the sulphuric acid to the lead peroxide plate, and from the lead peroxide plate through the external circuit to the lead plate; that is, from the electro-positive lead plate to the electro-negative lead

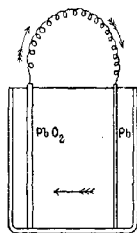
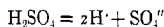


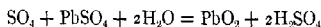
FIG. 32.

peroxide plate. This passage of current, and the chemical actions above set out, continue until the spongy lead and the lead peroxide are converted into lead sulphate. The solution at the end of the discharge, therefore, contains less sulphuric acid than at the commencement, because during discharge both plates use up sulphuric acid. Hence the specific gravity of the electrolyte in a discharged cell is always lower than in a fully

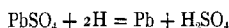
charged one. When an electric current is caused to pass in the opposite direction by connecting the + plate with the positive pole, and the - plate with the negative pole of a dynamo or other source of current, an opposite reaction takes place. The electrolyte for conveying the current consists, of course, of sulphuric acid.



The negatively charged  $\text{SO}_4^{''}$  ions have their charge neutralised at the + plate, but as  $\text{SO}_4$  is incapable of existence in the molecular condition, it reacts with the lead sulphate on the plate, and oxidises it to lead peroxide, with regeneration of sulphuric acid, thus—



The hydrogen ions give up their charge at the negative plate, and there reduce the lead sulphate to spongy lead, and reform sulphuric acid—



This chemical action—the conversion of lead sulphate into lead peroxide at the positive plate, and the formation of metallic lead at the negative plate—goes on until the whole of the lead sulphate is converted respectively into lead peroxide and spongy lead.

Further passage of the current now only causes electrolysis of the water to take place, with a consequent disengagement of oxygen gas at the positive plate, and hydrogen gas at the negative plate. Fig. 33 shows a cell manufactured by the Electrical Power Storage Company (E.P.S. cell), in which there are three positive plates and four negative plates. Accumulators always contain an odd number of plates, thus one of three plates would contain two negative plates and one positive plate, the

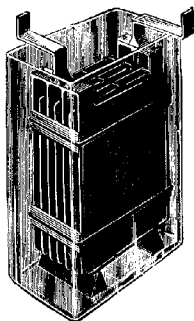


FIG. 33.

positive plate being placed between the two negative plates. A cell with seven plates would have four negative plates, and three positive plates. The greater the number of plates in a cell—that is, the greater the active surface—the higher the ampere-hour capacity of the cell. The E.M.F. is, of course, the same, whether there are three plates or twenty-one plates.

### Charging and Discharging Accumulators.

The sulphuric acid employed must be as pure as possible, and may on no account contain arsenic or chlorides, as these impurities are very detrimental to the cell. The acid must be diluted to the required specific gravity (1.15 to 1.17) before being placed in the cells. Charging should be commenced directly the

acid has been placed in the cells, and should, if possible, be continued uninterruptedly for about twenty hours. When it is not possible to charge in one run, the first charge should be at least for eight hours. In charging, a resistance should always be placed in series with the dynamo. When the cells are being charged for the first time, it is generally necessary, at the commencement, to shunt in a considerable resistance, because the cells themselves at the outset oppose very little resistance. As the cells become charged, and their E.M.F. rises, their resistance increases, and, in order to keep the charging current constant, it is necessary to take out some of the external resistance. The increased resistance of the cells as they become charged, is due to the back E.M.F. which they exert. The back E.M.F. for the first few minutes is, of course, practically nothing, but it gradually reaches 1.8 volts, and finally, when fully charged, is about 2.4 volts. During the first few hours of charging, the gravity of the acid sinks; but then it increases, until, when the cells are fully charged, it is about 1.2 to 1.22; the final gravity, however, depends, to a certain extent, upon the form of cells used and the gravity of the acid employed at the commencement.<sup>1</sup>

When the cells are nearly charged, gas commences to be given off at the plates—oxygen at the positive, and hydrogen at the negative. When fully charged, the cells gas freely, and the liquid becomes milky and opaque from the quantity of gas bubbles which it contains; the cells are then said to **boil**. This boiling is due to the electrolysis of the electrolyte, and although it does not hurt the plates, it should not be carried on for too long a period, because it wastes the electrolyte by spurning, and, if the current is excessive, may disintegrate the positive plates. It is advisable to coat all metallic connections, which might become injured by the acid spray, with vaseline, which can readily be painted on with a brush.

<sup>1</sup> The numbers here given refer to the Electric Power Storage Co. cells. Starting with a gravity of 1.17, the acid will, when the cells are fully charged, have reached a gravity of 1.2.

After the cells have been completely charged, the pressure at the terminals is generally 2.2 to 2.4 volts; it, however, soon falls to 2 volts, at which point it remains for some time, and then gradually falls as the cell is discharged. When it falls to 1.80 volts, the cells should be recharged, because they get out of condition if the voltage is allowed to fall too low. Even when the cells are not in use the E.M.F. slowly falls. It is not advisable to allow cells to remain without charging for a longer period than from four to six weeks, even when they are not in use. An accumulator should not be too rapidly discharged, otherwise the plates are very likely to buckle and get out of shape. This may cause a short circuit, which would ruin the cell. Neither should they be charged with a very high current density. When a very high density is employed, there is always a large amount of current wasted simply in electrolysis of the electrolyte.

When currents of sufficiently high voltage can be obtained, it is best to charge the cells connected up in series. The negative pole of the source of current is connected with the negative pole of the accumulator—*i.e.* with the lead pole—and the positive pole with the positive or lead peroxide plate. The E.M.F. of the charging current must be sufficiently high to overcome the back E.M.F. of the accumulator; this may be put as 2.5, therefore to charge one cell a potential of at least 3 volts must be employed. If six cells are connected up in series, the total back E.M.F. would be  $2.5 \times 6 = 15$  volts. (It is only towards the end of charging that the potential of a cell is as high as 2.5 volts.) A potential sufficient to overcome this back E.M.F. of 15 volts would require to be used in order to charge the six cells connected up in series.

By connecting the cells up in parallel, the internal resistance of the system is lowered, being very little more than that of only one cell. Now, the E.M.F., as has already been stated, of one cell is rather over 2 volts; therefore, in charging the cells connected in parallel, it is only necessary to use a voltage sufficient to overcome the back E.M.F. of, say, 2.5 volts. A potential of about 4 volts would therefore be amply sufficient to charge with.

Charging in parallel generally takes much longer than charging in series, because the available current is divided between all the cells, which are being charged. Thus, if six cells connected in series are being charged with a current of 12 amperes, then each individual cell is being charged at the rate of 12 amperes. But if the cells are connected in parallel, the 12 amperes is divided among the six cells, and each individual cell is being charged at the rate of 2 amperes per hour. In order to completely charge the cells in parallel, the current would therefore require to be passed six times as long as if they were connected in series. The total energy put into the cells would be the same, but in the one case it would be delivered more rapidly than in the other.

To a certain extent the condition of the cell can be told by noting the specific gravity of the electrolyte. As the cell discharges, the specific gravity of the electrolyte falls; this is because some of the sulphuric acid is used up to form lead sulphate. When the cell is in normal condition, the specific gravity rises again on recharging. If the cells have not been long in use, taking the specific gravity gives an excellent criterion as to their condition; but with cells which have been in use a long time without the acid being changed, too much reliance should not be placed upon the gravity alone. In any case, if the gravity is below 1.2 after the cell has been charged, probably something is the matter. The infallible proof of the condition of the cell is the E.M.F. After the cell has been charged and boiling has taken place, if the potential is below 2 volts, then the cell is out of order. As the charging of a cell becomes completed there is always a certain amount of gassing; this means that a certain amount of the electrolyte is being carried away by spraying. Therefore, after some time of use, partly from this reason, and partly from evaporation, the electrolyte requires replenishing. Generally the addition of *pure distilled* water is all that is necessary, because the main portion of the loss is through evaporation, but a certain quantity of acid is invariably lost through spraying.

The constant addition of water without adding fresh acid may

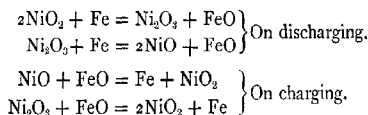
be the cause of the gravity being low; at the same time the voltage may be quite correct. If this is the case, a small quantity of strong *pure* sulphuric acid is added to bring the electrolyte up to the required specific gravity. The acid may be added to the cells *in situ*, but it is better to siphon off the electrolyte, bring up to the required gravity, and then return to the cell. Before interfering with the electrolyte, however, care should be taken to ascertain that the specific gravity really is low. If water has recently been added thorough mixing may not have taken place, and, after one or two charges, the gravity may be found to be quite correct. If both the gravity and the E.M.F. of the cell are low, even after a long charge, then the cell is said to be **sick**; probably in this case the positive plates will be of a reddish chocolate colour, instead of a dark brown, and the negative plates will very likely be a dirty whitish grey or may have large white patches of lead sulphate on them: the cause of the cell being out of order is due to **sulphating**. Generally speaking, charging alone will not put this right, and, if this is found to be the case, the cell should be taken down, the electrolyte siphoned off, and the negative plates scrubbed with a hard bristle brush under running water. Great care must be taken not to allow the least trace of grease to get upon the plates when they are being washed. The positive plates must not be allowed to dry, but should be well washed in running water; they must not, however, be scrubbed, because this would probably detach some of the lead peroxide. The cleaning of lead accumulators is not by any means an easy operation, and must be carried out with great care, otherwise the plates may be completely ruined.

The lead negative plates usually have a longer life than the positive peroxide plates. If the positive plates become damaged, it does not follow that the negative plates are also out of order, and the cell can be put in working order again by renewing the positives.

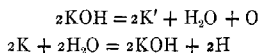
### Edison Storage Battery.

In the Edison storage battery the negative pole consists of iron; the positive pole is oxide of nickel, which is supposed to be nickel peroxide,  $\text{NiO}_2$ . The electrolyte is a 20 per cent. solution of caustic potash. Compared with the lead accumulator the voltage of this cell is comparatively low, being after recent charging 1.5 volt, but the normal discharge voltage is not much above 1.1 or 1.2 volt.

The reactions which take place may probably be represented by the following equations:—



The last two equations are brought about by the passage of the current through the electrolyte, hydrogen being liberated at the negative pole, which reduces the oxide of iron to the metallic state. Likewise oxygen is liberated at the positive plate, and oxidises the reduced nickel oxide back to nickel peroxide again—



At first sight it might be thought that, owing to its low E.M.F., the Edison cell could not compete with the lead storage cell. But it has certain advantages which go a long way towards compensating for its lower voltage. These are claimed to be—

- (1) Stability of the cell, absence of deterioration by work;
- (2) Large storage capacity per unit of mass;
- (3) Capacity for being rapidly charged and discharged, without buckling;
- (4) Capability of withstanding rough treatment;

The cell is coming into very considerable use for automobile work, especially in America; but so far, at any rate in England,

it has not been employed for laboratory purposes. It is very doubtful whether, at any rate for a long time to come, the alkaline accumulator will take the place of the lead battery. Although the cell may possess the above-mentioned advantages, the question as to its watt-hour capacity and as to the economy of charging are also important factors, and these have not yet been proved to be higher than those of the lead accumulator.

### **Electrolytic Rectification of Alternating Currents.**

It is found that when a plate of aluminium is made the anode in an electrolytic cell, at the moment of completing the circuit, the current flows as usual, but it rapidly becomes less and less, and in the course of a few seconds, if the E.M.F. is not more than 20 to 25 volts, the current ceases to pass. Obviously this cannot be due to polarisation, because the back electromotive force due to gaseous polarisation would not be much above 1 volt.

It is a well-known fact that aluminium readily becomes superficially coated with a film of oxide, and that this film exerts a protective action, preventing further oxidation from taking place. It is this superficial oxidation of aluminium which makes it so difficult to weld the metal or to plate other metals upon its surface. When aluminium is made the anode in dilute sulphuric acid, or in a sodium-phosphate solution, there is a tendency, on completing the circuit, for the aluminium to pass into solution. The moment, however, it commences to dissolve, the surface becomes coated with a film of hydrate or basic sulphate or phosphate, and this prevents actual contact between the solution and the aluminium. This film is a dielectric, so we get a dielectric polarisation, and the film acts as a condenser between the metal and the electrolyte. The dielectric polarisation almost absolutely prevents the passage of the current with potentials below 20 volts, but with higher voltages it partially breaks down, and a certain amount of current will pass. The resisting action



is also better at low temperatures, and is to a certain extent dependent upon the nature of the electrolyte. Grätz was the first to point out that this peculiar behaviour of aluminium might be employed to rectify alternating currents. In an alternating current there is a pulsation first in the one direction, and then in the other, or, in other words, the electrodes in a cell through which an alternating current is being passed are one moment negative, and the next moment positive. It is, therefore, not possible to conduct ordinary electrolysis with an alternating current. Although an aluminium plate cannot be employed as anode in electrolysis, for the reasons already explained, it can be used as a cathode, because in this case any protective coating, if it is produced, is removed by the reducing action of the hydrogen. As the alternating current consists of impulses first in one direction and then in the other, it should follow that, if an aluminium plate opposed to one of lead or carbon is placed in an electrolytic cell and connected with the alternating current, the positive phase will be unable to pass, but the

negative will have no such difficulty. This is actually found to be the case, provided the E.M.F. is not too high; but, of course, with a single cell 50 per cent. of the current would be lost. The best method of connecting up in order to obtain the maximum rectification and efficiency is shown in Fig. 34.

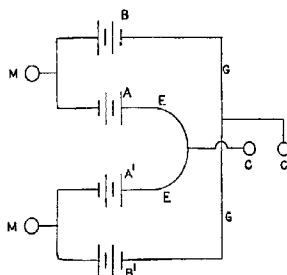


FIG. 34.

M, M are the terminals from the alternating mains, and n, n' and A, A' are four electrolytic cells. The long lines represent the aluminium plates, and the short lines lead or carbon. Now, when the current tries to travel through the cell B the negative impulse will pass without difficulty, but the positive will be prevented from passing by the aluminium plate; it will therefore

be thrown back, but will be able to pass through the cell A. The same applies to the current endeavouring to pass through B'; the positive will be thrown back, but will pass through A'. The negative currents from B and B' are united in the conductor GG, and the positive currents unite in the conductor EE. We have therefore, at the two terminals c and c, a continuous current, the terminal carrying the current from the aluminium plates being positive, and the terminal taking the current from the lead plates negative. The number of plates in the cells B, B' and A, A' depends upon the E.M.F. of the alternating current. As a matter of fact, it is not a question of the number of plates, but of the number of cells. Thus, as shown in the diagram, there are two long and two short lines in the cells; this really represents two cells connected together in series. One cell at ordinary temperatures will only rectify successfully if the E.M.F. of the alternating current does not exceed about 25 volts; at 0° the E.M.F. may be as high as 45 to 50 volts without the cell breaking down.

In some districts the alternating current is used for lighting; the current cannot therefore be employed for electrolytic purposes, or for charging accumulators. The current rectified as above explained will, however, be found quite satisfactory for charging accumulators. Absolute rectification, except perhaps at very low voltages, probably never takes place, there being always a greater or less amount of leakage. This leakage is due to a partial breaking down of the dielectric; at high temperatures the protective film seems to get more or less crystalline in structure, and then the leakage becomes very considerable. Presumably, when the negative impulse strikes the plate, sufficient breaking down, due to reduction of the film, does take place to allow the passage of the negative current, otherwise no current would pass in either direction. There is a certain voltage above which all dielectrics will break down; and under ordinary circumstances and at ordinary temperatures, with the film produced on the aluminium plate this is about 25 volts.

A very interesting phenomenon is noticed when an alternating current is passed through an electrolyte where one of the plates

is aluminium. The aluminium plate is noticed to phosphoresce, and its whole surface scintillates in a very beautiful manner. The

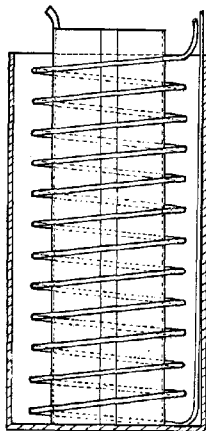


FIG. 35.

this is surrounded by a coil of lead or composition pipe, through which water circulates. The aluminium is made the one pole,

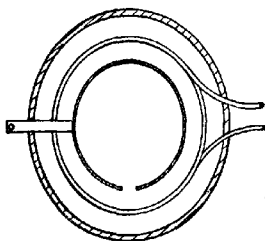


FIG. 36.

pipe. (The form of the apparatus is the same as shown in Figs. 35 and 36, except that the aluminium cylinder is closed and has a tube for ingress and egress of the cold water.) The efficiency of

electrode opposed to the aluminium does not show this peculiarity. Aluminium is not the only metal which prevents the passage of the positive electric current; magnesium, chromium, and indeed most metals have this property to some extent.

One difficulty in using electrolytic rectifiers is the great heating of the solution which takes place. Fig. 35 shows a sectional elevation and Fig. 36 the plan of one of the cells which have been successfully employed for charging accumulators at the Borough Polytechnic. The cell consists of a sheet of stout aluminium shaped into a cylinder; this is surrounded by a coil of lead or composition pipe, through which water circulates. The aluminium is made the one pole, and the lead pipe the other pole. The electrolyte consists of a cold saturated solution of ammonium phosphate,  $(\text{NH}_4)_2\text{HPO}_4$ .

More recently better results have been obtained by using a closed aluminium cylinder, and circulating cold water both through this cylinder and through the lead

the rectifier is very much greater at low than at high temperatures. Further, the aluminium plates last very much longer; it has been found that if the temperature is allowed to rise from  $30^{\circ}$  to  $40^{\circ}$ , the plates corrode away in the course of a few weeks. Whereas, when the electrolyte is maintained at a temperature below  $20^{\circ}$ , the plates appear to be very little attacked.

There is always considerable loss of energy in using these cells, unless the plates and solution are kept well cooled. By cooling the aluminium plates as above explained, over 90 per cent. rectification is readily obtained, *i.e.* the current efficiency is over 90 per cent., as shown by the amount of copper deposited from a copper coulometer. Even if considerable loss does take place, the conversion of an alternating into a continuous current by this means is a very great convenience.

#### LITERATURE.

L. Grätz, *Zeit. f. Elektrochem.* (1897), **4**, 67; K. Norden, *Zeit. f. Elektrochem.* (1899), **6**, 159 and 188; Livingston, Morgan and Duff, *Journ. Amer. Chem. Soc.*, **22**, 331; W. L. Hildburgh, *Journ. Amer. Chem. Soc.*, **23**, 300; C. Hambüchen, *Journ. Amer. Electro-chem. Soc.* (1903), **4**, 105; *Journ. Amer. Electro-chem. Soc.* (1904), **5**.

### Distribution of Current.

Fig. 37 represents diagrammatically an arrangement designed by the author which may be employed for distributing the current from storage cells. The arrangement here adopted is to avoid the multiplication of measuring instruments. The switch-board is designed to supply three circuits on three sides of a room. Each circuit may have any number of terminals to suit the desired number of students; but, of course, all the students working on the same circuit have to use the same number of cells. But by means of resistances the strength of the current which it is desired to employ can be regulated. The switch-board shown is connected with three circuits.

Each circuit is provided with an ammeter and voltmeter. Every working place is fitted with a separate set of terminals and a fixed resistance of about 20 ohms; heavier resistances can of course be

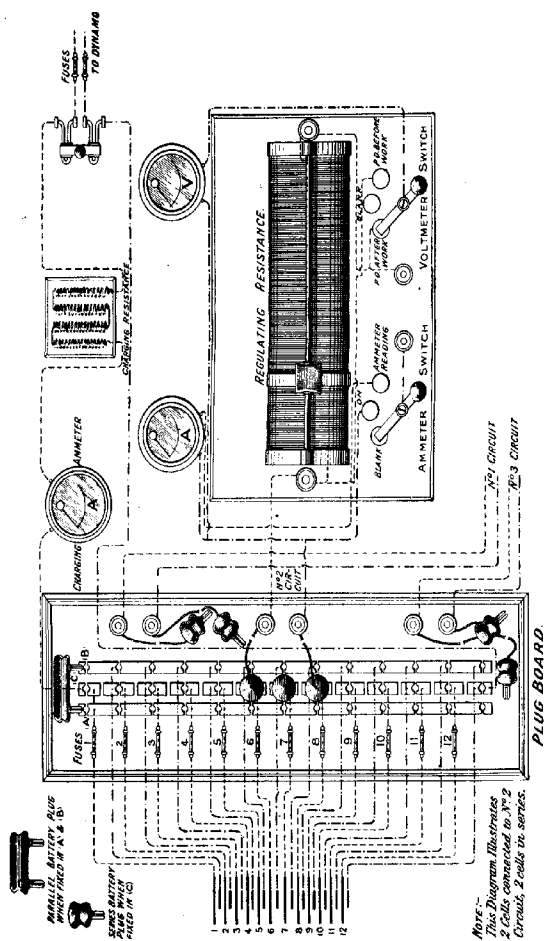


FIG. 37.

employed if required. The resistances are mounted, together with switches for the ammeter and voltmeter, on an enamelled slate base, and are fixed on the wall just above the benches. By means of one switch the student is enabled to take the ammeter reading, and having done so, to switch off and continue the electrolysis without keeping the instrument continually in the circuit—the resistance of the ammeter, being very low, is neglected. A second switch for the voltmeter is arranged in a similar manner. Thus, several students can use the same instruments without interfering with each other's work, and multiplication of these expensive pieces of apparatus is avoided.

**The Distributing Board** is arranged so that the cells may be connected up either in series or in parallel, or part in series and part in parallel. Further, although in the diagram there are only twelve cells, the whole number may be switched on to one circuit, ten on to another, and eight on to the third, and all circuits may be in use at the same time. Of course a smaller number of cells can be employed on any of the circuits when it is found desirable. The diagram shows the arrangement of the plug-board, and the manner in which it is connected with the accumulators, also the way in which the current is distributed to the several circuits.

From the diagram, which explains itself, it will be seen that a fuse is inserted in each of the leading wires from the battery, which protects the apparatus from damage in the event of an accidental short circuit taking place. Each cell is also separately fused.

It is not very often that it is necessary to have cells connected up in parallel, and in installations in which it may not be desired to have this arrangement, the distributing-board could be very much simplified by having only one row of plug holes. This would, at the same time, make the board very much cheaper. In the diagram, two cells are shown connected in series on to Circuit No. II. When the ammeter switch is moved on to the stud marked "On," the current passes through the decomposition cell which is in connection with the two terminals, but would

not be passing through the ammeter. On switching over to "Ammeter reading," the current passes through the ammeter and work. As soon as the student has taken his reading, he switches back to "On," and continues the work with the instrument thrown out. The voltmeter, which is of course on a shunt circuit, is so arranged that besides taking the P.D. of the work, the terminal E.M.F. of the circuit can also be taken.

**The Resistances.**—These are made from insulated "platinoid" wire, wound on asbestos-covered brass tubes. The advantage of winding on tubes is that a current of air passes through them and serves to keep the resistance cool. The contact is a double sliding one, and connection is made with the resistance wire by removing the insulation from the upper and lower surfaces of the coil. Each instrument has a resistance of about 20 ohms, and will carry a current of about 4 amperes without unduly heating. An ideal resistance at a moderate cost is a very difficult thing to obtain. With a resistance such as is here described, there is not much difficulty in cutting down by very small fractions of an ampere; but if it be required to carry a current of considerable density, and at the same time to reduce or increase the current by small fractions of an ampere, the best method is to employ a liquid resistance such as that shown in Fig. 41, p. 75. The method of distributing the current here described is simply given as an example of one which has been found in actual work to be very satisfactory. The method to be adopted in any laboratory will require to be modified to suit the special requirements of the work which it is intended to carry out.

**Pole Papers.**—It is sometimes necessary to test whether a wire is connected with the positive or negative pole. For this purpose turmeric paper moistened with a solution of sodium sulphate may be used; on placing the wires near together on the moist paper, a brown mark is produced where the negative wire touches it, due to the liberation of sodium. Pole papers often have phenolphthalein and sodium sulphate on them, and then the negative wire produces a pink mark.

## CHAPTER VI.

### REGULATION OF CURRENT.

IN all electro-chemical operations it is a matter of great importance to be able to control the quantity of current which is to pass through the electrolytic bath in a given time. Flow of water from a pipe is regulated by means of a tap, the amount of water which will flow depending upon how far the tap is turned on. The flow of the electric current is regulated by means of resistances; the greater the resistance switched into the circuit, the less the quantity of current that will flow.

In order to be able to compare different resistances, it is necessary to have a standard or unit of resistance. The unit of resistance is called the **ohm**. The ohm is defined as being *the resistance offered by a column of pure mercury 106.3 centimeters in length, having a uniform section of 1 square millimeter, at a temperature of 0° C.* The weight of this column of mercury is 14.4521 grm.

In practical working it would not be convenient to employ columns of mercury as resistances. Use is therefore made of the fact that different metals oppose different resistances to the passage of the electric current. Iron wire, for example, offers a very much greater resistance to the passage of the current than does copper wire. Resistances are often therefore made of iron wire. But for laboratory purposes it is more general to employ resistances made from certain alloys, such as platinoid or manganin.

**The resistance of a wire is proportional to its length and inversely proportional to its cross section. The**



**specific resistance** of a material is the resistance between two opposed faces of a cube of the substance, each edge of which is 1 cm. in length. The appended table gives the specific resistances of a number of substances, measured in microhms (a microhm is the millionth of an ohm, *i.e.*  $10^{-9}$  ohm). The measurements given have been taken at  $0^{\circ}$ .

TABLE VII.

Substance.	Specific Resistance.	Resistance of 1 metre of 1 sq. mm. cross section.
Silver, hard drawn	1.468	0.01468
Gold, annealed	2.053	0.02053
Copper, annealed	1.560	0.01560
„ hard drawn	1.629	0.01629
Aluminium, annealed	2.905	0.02905
Iron, annealed	9.693	0.09693
Platinum, annealed	9.035	0.09035
German silver	20.886	0.20886
Manganin	46.700	0.46700
Platinoid	41.731	0.41731

**Temperature Coefficient.**—When the current passes through a wire, the wire becomes hot; but a hot wire offers a greater resistance to the passage of the current than a cold wire, therefore the resistance is more or less variable, the variation depending upon the temperature co-efficient of the metal or alloy. The great advantage of an alloy such as platinoid is, that it has a very low temperature coefficient. For instance, the conducting power of pure iron falls by 39.2 per cent. when it is heated from  $0^{\circ}$  to  $100^{\circ}$ ; whereas, through the same range of temperature, platinoid only falls by 2.09 per cent. The temperature coefficient, therefore, per degree is respectively 0.392 and 0.0209. The appended table gives the temperature coefficient per cent. of certain metals and alloys.

TABLE VIII.

Metal.	Increased resistance per cent. 0° to 100° C.
Silver, annealed	40.0
„ hard drawn	40.0
Copper, annealed	42.8
„ hard drawn	38.8
Iron, pure	39.2
„ annealed	62.5
Aluminium	39.0
Platinum	36.7
Gun metal	39.2
German silver	4.4
Platinoid	2.09

### Ohm's Law.

*Ohm's Law states "that the current strength varies directly as the electromotive force and inversely as the resistance;"* or we may say—the ratio between the electromotive force and the current shows the resistance. Thus, if E represents the electromotive force, C the current, and R the resistance, then we have—

$$\frac{E}{C} = R$$

Therefore knowing the electromotive force and the resistance, we can find the current strength of a circuit.

$$C = \frac{E}{R}$$

I. For example, suppose the electromotive force of the batteries in a circuit is 12 volts, and the resistance is 9 ohms, what current will pass through the circuit?

$$C = \frac{12}{9} = 1.33 \text{ amperes}$$

II. Similarly, if the current and the resistance are known, we can calculate the electromotive force. If the resistance of a

circuit is 15 ohms, and the current 1.5 amperes, what is the E.M.F.?

$$E = 1.5 \times 15 = 22.5 \text{ volts}$$

III. And the resistance  $R$  can be calculated when we know the E.M.F. and the current. If the E.M.F. is 16 volts, and the current 0.5 ampere, what is the resistance?

$$R = \frac{16}{0.5} = 32 \text{ ohms.}$$

As a rule, the calculations are not quite so simple as the above, because in any circuit the total resistance is made up of a number of smaller resistances. There are the leads which convey the current; these represent a certain resistance. The various connections, especially if the junctions are not well cleaned, are sure to cause a greater or less resistance. Then there is the known resistance for regulating the current. Finally, there is the unknown resistance of the electrolytic cell, which may be continually varying, either owing to polarisation or to changes in the concentration of the electrolyte and to heating effects.

**Resistance of the Electrolytic Cell.**—It is sometimes useful to know the resistance of the electrolytic cell. This we are able to calculate from Ohm's Law. What we require to know is the current which is passing, and the drop in potential between the electrodes.

For example, in an electrolytic cell in which the electrolyte consisted of a 15 per cent. solution of copper sulphate and the electrodes were both of copper, a current of 2.5 amperes was found to be passing. The drop in potential between the electrodes was 3.2 volts, therefore the resistances of the cell was—

$$R = \frac{3.2}{2.5} = 1.28 \text{ ohms.}$$

The above example was purposely taken, because in such a cell, where both the electrodes are of the same metal, and the

electrolyte is a salt of the metal, there are no polarisation effects. Generally, however, there is a greater or less back E.M.F. produced by polarisation.

**Cell Polarisation and Back E.M.F.**—Polarisation always produces a back electromotive force, and in order to calculate correctly the resistance we must measure the back E.M.F. of the cell. This may be done by connecting a voltmeter across the two electrodes. The voltmeter will show the apparent drop in potential between the electrodes. Now switch off the current, the voltmeter will recede back until it stops for a short time at a point somewhere above zero, and then gradually fall back until it comes to zero. The position to which it fell in the first instance is the **polarisation voltage**. An example will make this clear. In a cell which contained a solution of sodium sulphate both the anode and cathode were of lead. After the current had been passing for some time the voltmeter was shunted across the electrodes, and was found to read 4·8 volts; the ammeter at the same time showed a reading of 3 amperes. The current was then cut off; the voltmeter fell to 2 volts, where it remained for a short time, and then gradually fell to zero. The back E.M.F. was therefore 2 volts, which was opposed to the passage of the current. Thus the resistance of the cell due to the back E.M.F. was—

$$R = \frac{4.8 - 2}{3} = 0.93 \text{ ohms.}$$

### Some Forms of Resistance.

A simple form of resistance is shown in Fig. 38. It consists of coiled lengths of wire fastened on to a frame. By moving the switch on to different studs, various amounts of resistance can be thrown in. Each length of wire generally represents a known resistance: for example, each wire may represent a resistance of 1 ohm; therefore, when the switch is on the fifth stud, there will be a resistance of 5 ohms thrown in. When heavy currents are

employed, the resistance wire may become very hot, and the wire is then generally mounted on an iron frame fixed upon a slate base.

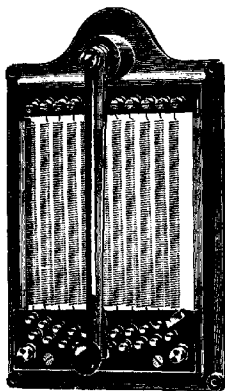


FIG. 38.

Fig. 39 shows another form of adjustable resistance. It is made of insulated platinoid wire wound upon an asbestos-covered brass tube. Contact is made by sliding the brass rubber A along the bar B—connection being made with the resistance wire by removing a portion of the insulation from its upper surface.

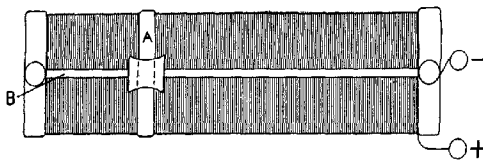


FIG. 39.

Fig. 40 illustrates another form of adjustable resistance which can be made for carrying still heavier currents.

When it is necessary to cut a heavy current down, and to regulate by small fractions, it is best to pass the current through a liquid resistance. Fig. 41. This may be simply a glass or, better,

an earthenware trough, containing dilute sulphuric acid or caustic soda (the concentration of the electrolyte depending upon the resistance required), and having two lead plates as electrodes, when sulphuric acid is used, or nickel plates when caustic soda is the electrolyte. The resistance is regulated by moving the two plates AA either nearer together, to increase the current; or further apart, to decrease the current.

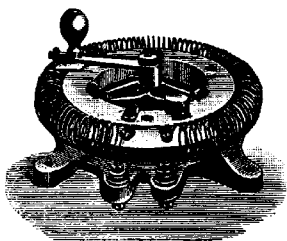


FIG. 40.

The only objection to this form of resistance is that, if the current is very heavy, the solution becomes hot and evaporates away. If, however, one of the electrodes consists of a coil of

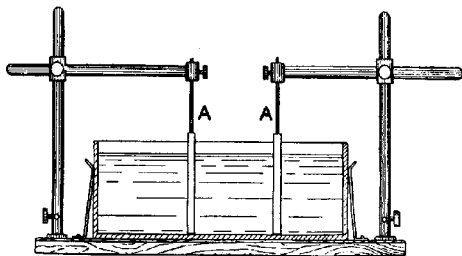


FIG. 41.

lead pipe, through which cold water is allowed to flow, the heating of the solution is very much reduced. Many other forms of resistance might be described, but for general laboratory work the ones here described should be quite sufficient. The class of resistance employed will depend upon the kind of work for which it is required, and to a great extent upon the personal experience and likes of the experimenter.

## CHAPTER VII.

### *APPARATUS FOR ELECTROLYSIS.*

IN almost all electrolytic depositions it is necessary to employ platinum anodes and cathodes. The cathodes are either in the form of basins, cylinders, cones, or flags. Basins have perhaps been more largely used than any other form of electrode, but they are extremely expensive, and have really no advantage over a gauze cylinder or flag electrode.

When a basin is employed, it should be of sufficient capacity to hold from 150 to 180 c.c. of solution. The best form of anode is of platinum wire coiled concentrically, as illustrated in Fig. 42. In using the basin a stand of the following construction will be found very convenient (Fig. 43). The base of the stand is of slate or marble, and the brass rod which conveys the - current is hollow; through this brass rod an insulated wire for carrying the + current passes, and is connected at the top of the rod to an insulated binding-screw, and at the bottom with the binding-screw fixed on to the slate base. The arm for holding the anode is insulated from

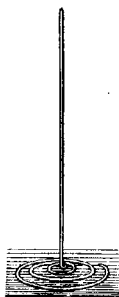


FIG. 42.

the upright brass rod by means of a piece of ebonite. The ring which supports the basin has three little platinum points at equal intervals on its circumference; on these the basin rests, thus ensuring good contact. The + pole of the source of current is connected with the binding-screw fixed in the slate base, and the negative pole with the binding-screw marked -.

During the course of electrolysis—especially when hot solutions are used—it often happens that the volume of the solution falls below the edge of the deposited metal, which may then become oxidised and lead to incorrect results. In Fig. 44 is shown an arrangement for getting over this difficulty. A small beaker is held in a ring which is placed upon the upper part of the rod of the

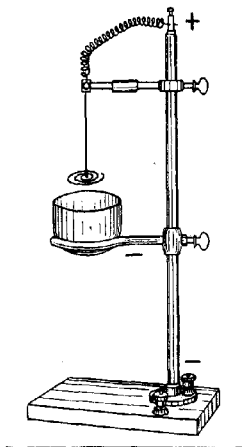


FIG. 43.

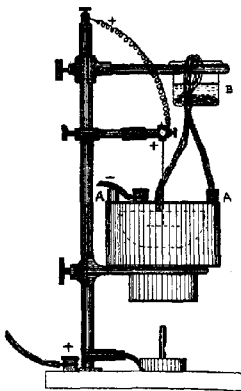


FIG. 44.

stand; the beaker is filled with distilled water, and has hanging over its side a piece of lampwick. One end of the wick is in the water, and the other end is twisted round the anode; the water slowly siphons over from the beaker, and by arranging the number of threads in the wick and the height of the beaker from the basin, the water can be made to flow into the basin as rapidly as it is evaporated or electrolysed away. If it is desired to keep the solution acid, as, for example, in the analysis of zinc by the oxalate method (p. 119), then the beaker is filled with dilute oxalic acid.



### Heating Platinum Basins during Electrolysis.

Special precautions are necessary for heating platinum basins. The flame of the burner may on no account come in contact with the basin, as this causes the platinum to become dull, probably from formation of carbide. Another drawback to direct heating is, that the heating may become too local, and this may cause the deposit to scale off; the deposits are almost certain to scale if the solution is boiled. In order to give a diffused heat, a piece of sheet asbestos may be placed upon a ring under the basin, or

a very small flame may be placed some 4 cm. below the basin. Perhaps the best method is to use a water-bath of the form depicted in Fig. 44. The bath really acts as an air-bath, as it is so arranged that the basin shall not come in contact with the water, the only openings to the bath being the two small funnels A, A. Three small pieces of platinum wire are soldered into the copper cavity, and on these the basin rests. There is an air space of about 2 cm. all round the basin.

It will be found that if the bath be filled with a mixture of equal parts of water and glycerin, that this mixture can be heated to a temperature of about  $130^{\circ}$  without boiling, and that then the temperature of the solution in the platinum basin will be between  $50$  and  $60^{\circ}$ .

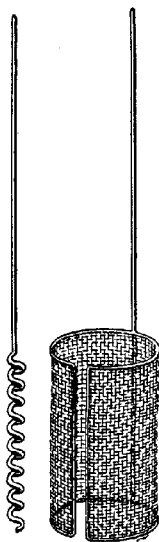


FIG. 45.

Fig. 45 shows a cylindrical gauze electrode with its anode. Cylindrical electrodes

other than gauze cannot be recommended, because of the great unevenness of current density, the metal being mainly deposited upon the inside of the cylinder, and only to a limited extent upon the outside.

Perhaps the best form of electrode is the flag form shown in Fig. 46; the cathode is in the form of a flag and is made of platinum gauze, which should be sufficiently stout to permit of being sand-blasted; it is held rigid by means of a platino-iridium frame (10 per cent. iridium); the frame, which is roughened by means of the sand-blast, has a stout piece of iridio-platinum wire welded on to it. The wire is for holding the electrode in position during analysis. The loop near the top of the wire is for hanging the electrode on the balance.

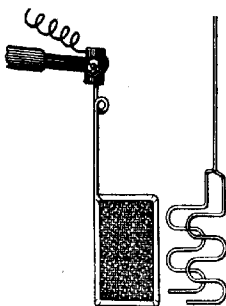


FIG. 46.

The anode is made of platinum wire, and is bent upon itself in such a way, that when it is placed into position for electrolysis, as illustrated in Fig. 47, an even current density is obtained on all parts of the cathode. The distance between the two sides of the anode is 2.5 cm., therefore when in position it is 1.25 cm. distant from each side of the cathode.

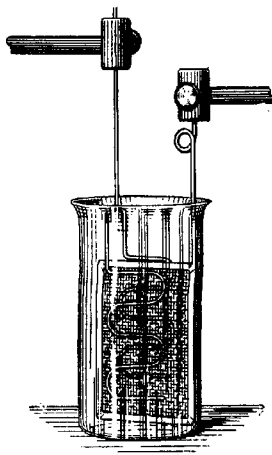


FIG. 47.

The cathode is 6 cm. high and 4.3 cm. wide, and the length of the supporting wire is 7.5 cm., the loop being 2.5 cm. from the end. As the anode is opposed to both sides of the cathode during electrolysis, it follows from the above measurements that the total cathode surface is 50.4 sq. cm., that is, practically

half a square decimeter, which, as the current density (C.D.) for analytical purposes is generally calculated per square decimeter of surface, is a very convenient size. It is not essential for the cathode to be made of gauze—in many cases sheet platinum is quite as useful; but for metallic deposits which are inclined to exfoliate, such as bismuth and antimony, the gauze is more satisfactory; it is also very useful for mercury and for peroxide deposits. The gauze should not be too fine; the finest that I have found satisfactory is about 80 to 90 meshes to the square centimeter. When it is too fine there is a tendency for hydrogen to collect upon the surface and thus cause polarisation.

The weight of the cathode, when made of platinum sheet, is about 14.5 gm. If thinner platinum is employed, the weight can be reduced to 8 gm., but it is found better not to make them of very thin platinum, because then they are too fragile, and there is a tendency for the deposits not to adhere well at the edges. The weight of the gauze electrode is about 15 gm.

**Current Density (C.D.)**, as already stated, is the intensity of current per unit of surface. Thus, if the surface is 1 square decimeter, and the current is 2 amperes, we say that the C.D. is 2 amperes. If, however, the electrode was only 0.25 of a square decimeter, then, if the current was 2 amperes, the C.D. would be 8 amperes. The current densities given in this book always represent the C.D. per square decimeter.

### Rotating Electrodes.

The rate of deposition of a metal from its solutions is very much accelerated, and a higher C.D. can be employed, when the cathode is kept in rapid rotation. In Fig. 48 is shown a rotating cathode, and the arrangement employed for rotating it. The support for the cathode consists of a gun-metal arm, the end of which is drilled to allow a spindle to pass. This spindle carries a small chuck (such as is used for fixing small drills) which is used for holding the rotator. The grooved pulley, which is fastened on to the upper end of the spindle, bears on the

top of the arm, which is ground smooth. The whole arrangement is driven by means of a belt from a water-turbine or electric motor. This arrangement is found to give very perfect contact and to work with very little friction. The parts should only be slightly lubricated, the best lubricant being a mixture of graphite and oil.

The cathode, as is seen from the figure, is a small sand-blasted cylinder, of platinum gauze, which has a combined surface of about 25 cm. The anode is in the form of a double circle of stout platinum wire, and has four little baffles placed at intervals round it, to prevent the liquid from rotating

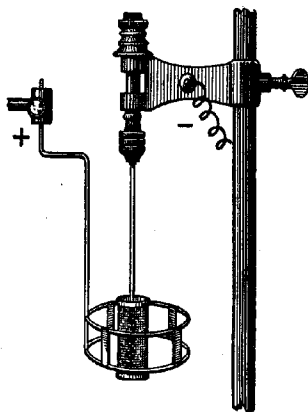


FIG. 48.

with the cathode. A double coil of stout platinum wire serves equally well. Of course for peroxide deposits the rotating electrode would be the anode. A cylinder of sheet platinum also gives very good results, but in this case very little metal is deposited upon the inner surface. Longitudinal slits, however, partially get over this difficulty, but with gauze as shown in the figure the deposition is practically equal inside and outside. Not only are the metals deposited more rapidly by the use of a rotating cathode, but the deposits are generally exceedingly bright and have a magnificent burnished appearance; this is especially the case when cobalt is deposited from a solution containing ammonium tartrate. When the cathode is of gauze the brilliancy of the deposit is not so marked as when a smooth cathode, such as that described by Gooch, which consists of a platinum crucible, is employed.

### **Preparation of Electrodes.**

In all forms of analysis, cleanliness of apparatus is a matter of importance; if possible, it is even more important when electro-chemical methods are employed. The slightest trace of grease or dirt upon the cathode must be avoided, otherwise the deposit will be patchy, and often non-adherent. In order to clean the electrodes they should first be heated in nitric or hydrochloric acid, or warmed with a mixture of sulphuric acid and potassium dichromate. They should then be thoroughly washed under the tap, and afterwards with distilled water. If they still appear greasy, they may be washed with caustic alkali, well rinsed, and finally heated to redness in the bunsen flame or by means of the blowpipe. It is not necessary to cool them in a desiccator before weighing. It is, however, generally speaking, better—as far as possible—to allow the electrodes to cool for the same length of time before weighing, say twenty minutes or half an hour. After ignition the cathode surface must on no account be touched with the fingers, because the grease of the fingers might be sufficient to spoil the metallic deposit.

Before igniting platinum, great care must be taken that every particle of the metallic deposit has been removed; otherwise, on heating, an alloy may be formed which will spoil the apparatus. On no account may platinum be heated in a smoky flame, as this dulls the surface and forms a carbide. From time to time, if the platinum becomes dull, it may be necessary to polish it with a little *very* fine sand or pumice powder; when this is carefully done, the weight of the platinum is not appreciably altered.

PART II  
ELECTRO-CHEMICAL ANALYSIS



## CHAPTER VIII.

### *ELECTRO-CHEMICAL ANALYSIS.*

ALTHOUGH so far back as 1801 Cruikshank suggested the employment of the electrical current for analytical purposes, and in 1812 Fischer recommended it for the detection of small quantities of arsenic, the careful and successful study of electro-chemical methods is of comparatively recent date. Yet while many processes of great importance and usefulness have been discovered, it must not be supposed that it is possible to carry out analysis solely and entirely by electrical methods. In a great many cases pure salts of the metals may be very readily and conveniently analysed electrically, yet it often happens that it is much more convenient to employ methods of separation which are purely chemical. For example, although silver and copper can comparatively readily be separated from each other by variations of electrical potential, still, generally speaking, it is better to first separate chemically and then to electrolyse the two separately. Theoretically speaking, it should be possible to separate practically all the metals by carefully regulating the electromotive force, because, as Magnus stated in 1856, "in every mixed electrolyte there is a certain limit of intensity, at which only one of the components will be decomposed." But it is usually found in mixtures, unless the limit at which the various constituents are decomposed lies comparatively far apart, that the one metal upon being deposited brings down a certain quantity of the other metal, and that therefore a complete separation does not take place.

In studying electro-chemical methods of analysis, it is usual and advisable, in the first place, to investigate the behaviour of



solutions of pure salts, before endeavouring to separate mixtures of the metals.

The metals may be roughly grouped according as to whether they are deposited in acid, alkaline, or neutral solutions or as to whether they can be obtained as cathode or anode deposits. In any case, however, the grouping is only very relative, because as a rule metals which can be deposited from acid solutions may also be deposited from solutions which are alkaline or neutral. No special attempt will therefore be made to follow out any particular line of grouping, but as far as possible those metals will be placed first which are the most easy to deal with.

### **Copper.**

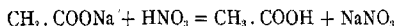
Copper may readily be deposited from solutions which contain considerable quantities of nitric or sulphuric acid. But good deposits can also be obtained from cyanide solutions, and it is possible to employ solutions containing an excess of ammonia.

**Nitric Acid.**—Dissolve about 1 grm. of copper sulphate or other copper salt in about 140 c.c. of water, and add 5 to 10 c.c. of nitric acid (sp. gr. 1.42) to the solution, that is, from 8 to 10 per cent. of the acid. If the flag electrode (p. 79) is employed, usually about 120 c.c. of water is sufficient, in which case proportionately less nitric acid must be used. The solution may either be electrolysed at ordinary atmospheric temperature, or heated from 45–50° C.; in the latter case, the time required for the complete deposition of the metal is considerably lessened. The best C.D. to employ is from 0.8 to 1.2 amperes, with an E.M.F. of from 2 to 2.8 volts. A bright red film will be seen to flash across the cathode almost immediately the circuit is completed. In cold solutions, from 2½ to 3 hours will be required to completely deposit the metal; with hot solutions the rate of deposition is considerably accelerated.

**End Reaction.**—In order to ascertain whether all the metal has been deposited out, the level of the solution may

be raised—if a basin is being used—a few millimetres by pouring in distilled water; if, after about 10 minutes, no copper is deposited upon the clean platinum surface thus covered, the electrolysis may be considered as finished. In other cases, where a flag or cylindrical electrode is employed, withdraw about 1 c.c. of the solution by means of a pipette, transfer to a test tube, make alkaline with ammonia, then acid with acetic acid, and add a few drops of potassium ferrocyanide; the formation of a brown precipitate or colouration shows that there is still some copper left in the solution, in which case, of course, it is necessary to continue the electrolysis until, on further testing with the reagent, no colouration is produced.

**Washing the Deposit.**—As the electrolyte contains an excess of nitric acid in which the copper deposit is readily soluble, it is recommended by some writers to siphon off the solution and, at the same time, to run in distilled water; by others, to add excess of sodium or ammonium acetate to fix the free nitric acid.



These precautions, however, are not necessary, provided the operator is a fairly quick manipulator. The author prefers to have a basin of water ready at hand, and an empty beaker or basin; then, as soon as the circuit is broken, to pour the solution into the empty vessel and at once rinse out in the basin of water, after which to rinse out twice with distilled water, and, finally, with about 10 c.c. of absolute alcohol;<sup>1</sup> then, to dry in the steam oven for about ten minutes—or the dish may be dried by carefully holding above the flame of a bunsen burner. When a flag or cylindrical electrode is used, it should, on breaking the circuit,

<sup>1</sup> The alcohol used should be of good quality, and must leave no residue on evaporation. Instead of using absolute alcohol, methylated spirit, which must contain no mineral oil, can be employed. It should, however, be first purified by allowing it to stand over caustic soda for twenty-four hours and then distilling. Quicklime is now added to the distillate, and, after standing for another twenty-four hours, the methylated spirit should again be distilled directly from the quicklime, without first filtering. Alcohol treated in this way is almost absolute.

be dipped into water, rinsed with distilled water, and finally with alcohol; this is best done with a wash bottle, the electrode being held over a beaker in order that the alcohol may not be lost. Or it may be dipped in a beaker of alcohol.

The deposit obtained from nitric acid is bright red, and generally has a more or less crystalline appearance. If the C.D. has been too high the deposit will very likely be "burnt" and have a brownish appearance, and may be of a powdery nature and non-adherent. When it is desired to electrolyse over-night, and this is often found very convenient, a C.D. of from 0.2 to 0.3 of an ampere is used. It is generally advisable in this case to add more nitric acid, because owing to the reducing action of the hydrogen liberated at the cathode, the nitric acid becomes converted into ammonia. This formation of ammonia causes the deposit to be spongy and of a bad colour, when it is difficult to wash and weigh. For running over night about 2 c.c. extra of nitric acid should be added for every 100 c.c. of solution.

In commercial copper analysis, it often happens that there are small quantities of arsenic or antimony present in the metal to be analysed. When they are present there is a tendency for traces of these elements to be deposited along with the copper. If any considerable quantities of antimony or arsenic have been deposited their presence can generally be noticed by the deposit not being so bright and having a dark appearance (the darkness due to the deposition of antimony and arsenic is not the same as the "burnt" amorphous appearance produced by employment of excessive current densities). In order to eliminate this source of error, the electrode with the copper deposit is heated to dull redness for a short time, by which means the copper is converted into oxide, and the antimony and arsenic are volatilised. The copper oxide is then dissolved in nitric acid, and again electrolysed. Hollard and Bertiaux find that the addition of a small quantity of ferric sulphate prevents the deposition of the arsenic. The addition of small quantities of a lead salt prevents the deposition of the antimony. Where there are very large quantities of antimony and arsenic present, it is better to separate them by chemical

means before electrolysis. Tin, bismuth, mercury, and especially silver, also have a tendency to come down in small quantities, but they are much less likely to do so if a considerable excess of nitric acid is employed.

**Sulphuric Acid.**—The deposit obtained when sulphuric acid is employed as the electrolyte is not nearly so brilliant as when nitric acid is used, but is generally of a dull red appearance and has no crystalline surface. The analytical results, also, are hardly as good and reliable as in the preceding case: this method is very often employed for commercial analysis.

The amount of sulphuric acid used should be from 7 to 10 per cent., and should not exceed the latter quantity. When concentrated sulphuric acid is employed, from 4 to 5.5 c.c. would represent the above quantities. About 1 gm. of the copper salt is sufficient. With a current of 0.8 ampere at atmospheric temperature the separation is completed in the course of two or two and a half hours. At temperatures of from 50 to 60° the separation is considerably accelerated. The E.M.F. required is from 2.5 to 3.2 volts. The C.D. should not be allowed to exceed 0.5 to 0.8 ampere, otherwise the deposit is spongy and dark and non-adherent. In any case, owing to the tendency to formation of spongy copper, this method is not so satisfactory as the preceding.

If a small quantity of hydroxylamine sulphate is added to the solution, the deposit is much brighter, and less inclined to be pulverent. When it is desired to carry out the deposition overnight by use of a C.D. of from 0.1 to 0.2, the addition of 0.5 gm. of hydroxylamine sulphate is sufficient, and it is not necessary to add more than 3 c.c. of concentrated sulphuric acid; but for ordinary work, when currents of from 1 to 1.2 amperes are employed, about 1 gm. of hydroxylamine sulphate and about 5 to 6 c.c. of sulphuric acid should be used. Classen also recommends the employment of small quantities of urea to prevent the formation of a spongy deposit. Although it undoubtedly has this effect, its use is not to be recommended, because small quantities of carbon and traces of platinum, from the anode, always contaminate

the copper deposit, and thus the results obtained have a tendency to be too high. The exact action of these substances is not clearly understood. It is also as well to take similar precautions as those already described in breaking the circuit and washing the deposit.

**Potassium Cyanide.**—Of all the copper deposits, the most beautiful is that obtained from solutions containing potassium cyanide. The colour of the deposited metal is pinkish red and beautifully smooth. But from other points of view the deposition from cyanide solutions has no advantage over the deposits obtained from acid solutions. In carrying out this process, the copper salt is dissolved in about 30 or 40 c.c. of distilled water, and then a freshly prepared solution of potassium cyanide added. A greenish yellow precipitate is at first produced, but, on adding more of the solution of potassium cyanide, it dissolves, a colourless or straw-coloured solution being produced. Slightly more potassium cyanide than is necessary to dissolve the precipitate should be used, but any considerable excess must be avoided. Generally speaking, from 1 to 1.5 grams of potassium cyanide should be used for every gram of copper salt taken.

The C.D. employed should be from 0.8 to 1.2 amperes. The E.M.F. required in cold solutions will be found to be about 5 to 6 volts; in warm solutions, from 4 to 5 volts. The whole of the copper is deposited in 2 to 2½ hours.

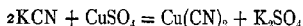
#### LITERATURE.

Gibbs, *Zeit. f. Anal. Chem.*, III. 334; Boisbaudran, *Bull. Soc. Chim.*, 1867, 468; Merrick, *Amer. Chem.*, II. 136; Herpin, *Zeit. f. Anal. Chem.*, XV. 335; Wrightson, *Zeit. f. Anal. Chem.*, XV. 299; Classen, *Ber.*, XIV. 1622 and 1627; Classen and von Reiss, *Zeit. f. Anal. Chem.*, XIV. 246; Hampe, *Berg. und Hütten Zeit.*, XXI. 220, and XXV. 113; Riché, *Zeit. f. Anal. Chem.*, XXI. 116; Rüdorff, *Ber.*, XXI. 3050; Luckow, *Zeit. f. Anal. Chem.*, VIII. 23; Warwick, *Zeit. f. Anorg. Chem.*, I. 285; Smith, *Amer. Chem. Soc.*, XII. 329; Croasdale, *Journ. Anal. Chem.*, V. 133; Foote, *Amer. Chem. Journ.*, VI. 333; Meeker, *Journ. Anal. Chem.*, VI. 267; Classen, *Ber.*, XXVII. 2060; Heidenreich, *Ber.*, XXIX. 1585; Regelsberger, *Zeit. f. Angew. Chem.*, 1891, XVI. 473; Oettel, *Chem. Zeitung*, 1894, 879; Fejnberger and Smith, *Amer. Chem. Soc.*, XXI. 1001; Wagner,

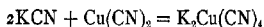
*Zeit. f. Elektrochem.*, II. 613; Foerster and Seidel, *Zeit. f. Anorg. Chem.*, XIV. 106; Revay, *Zeit. f. Elektrochem.*, IV. 313; Hollard, *Compt. Rendus*, **123**, 1003; Kollock, *Amer. Chem. Soc.*, XXI. 923; Richards and Bisbee, *Amer. Chem. Soc.*, **1904**, **28**, 530; Hollard and Bertiaux, *Bull. Soc. Chim.*, 1904 [iii.], **31**, 900.

### Hittorf's Explanation of Electrolysis of Complex Cyanides.

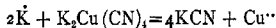
When excess of a solution of potassium cyanide is added to a solution of a copper salt the reaction takes place in two stages; in the first place, a greenish yellow precipitate of copper cyanide is produced; thus—



but, on adding a further quantity of the cyanide solution, the copper cyanide dissolves with formation of a complex salt **potassium cupricyanide**.



Now, potassium cupricyanide is ionised into the cations  $2\text{K}$  and the anion  $\text{Cu}(\text{CN})_4^{--}$ , therefore on electrolysis the first process will be for the  $\text{K}$  ion to be transported and given up at the cathode, while the complex anion  $\text{Cu}(\text{CN})_4^{--}$  will migrate to the anode. This anion  $\text{Cu}(\text{CN})_4^{--}$ , however, is not stable in the molecular state, *i.e.* when deprived of its electrical charge, but is split up into  $2(\text{CN})$  and  $\text{Cu}(\text{CN})_2$ . In the mean time the potassium liberated at the cathode has reacted with some of the undecomposed potassium cupricyanide, which is then decomposed according to the equation—



The copper thus liberated travels in the ionic state to the cathode, where it is deposited, and the regenerated potassium cyanide dissolves the  $\text{Cu}(\text{CN})_2$  which has been deposited upon the anode regenerating the salt  $\text{K}_2\text{Cu}(\text{CN})_4$ . As, beside the fact of this liberated potassium cyanide, there is always excess of cyanide present, and as in any case the interactions are momentary, there is never a deposit of cupricyanide perceptible at the anode.

Many other methods for the quantitative deposition of copper have been devised. Thus, for example, electrolysis of solutions containing excess of ammonium hydrate, together with ammonium sulphate or, better, nitrate, but the depositions in this case are not nearly so satisfactory as those already given, neither is there anything to be gained by using Classen's oxalate method. The ammonia method, as improved by Oettel, may sometimes be found useful in separation of copper from other metals, and when chlorides are present.<sup>1</sup>

### Nickel.

Nickel is a metal which it is impossible to deposit from solutions containing free mineral acids or excess of organic acids. Although a great number of methods have been suggested for the electrolytic deposition of nickel, only a very few of these are really of practical importance. Probably the most useful method is that of Fresenius and Bergmann, in which the double sulphates of ammonium or potassium and nickel, together with excess of ammonia, are used. The nickel salt is dissolved in water, and then about 4 or 5 grams of ammonium sulphate, also dissolved in water, added, and about 30 to 35 c.c. of ammonium hydrate (sp. gr. 880); the solution is then made up to the required bulk. If more than about 1 gm. of nickel salt is used, the amount of ammonium hydrate must be increased. As, however, the use of large quantities of ammonium hydrate contaminates the atmosphere of the laboratory, it is better to employ smaller quantities of the salt rather than to increase the volume of ammonia; on the other hand, if too little ammonia is used, the nickel deposit has often a dark brownish appearance, and there is a tendency for nickel oxide to be deposited at the anode. Nitrates should not be present; as their presence very considerably retards the rate of deposition of the nickel. When nitrates are present, the nickel salt should be evaporated down to dryness with a little sulphuric acid, in order to expel the nitric acid, before being electrolysed.<sup>2</sup>

<sup>1</sup> *Zeit. f. Electrochem.*, 1894, 142.

<sup>2</sup> *Zeit. f. Anal. Chem.*, XIX. 329.

The solution may be electrolysed at normal temperature with currents from 1 to 1.5 amperes; the E.M.F. will be from 2.8 to 3.5 volts. Under these conditions the electrolysis will be complete in about two and a half hours. When the solution is warmed to from 45° to 50°, one and a half to two hours will be required. The appearance of the deposit varies from a silver grey to that of burnished platinum; sometimes it is difficult to tell where the nickel deposit leaves off and the platinum begins.

**End Reaction.**—When the solution has become colourless, withdraw about 1 c.c. by means of a pipette, and add a few drops of sulphuretted hydrogen water; if a brown coloration is produced, all the nickel has not been deposited. The electrolysis is then carried on until, on further testing, no coloration is produced. Yellow ammonium sulphide should not be used in this test, because the yellow colour often masks the brown colour of the nickel sulphide. Neither should only a single drop of the electrolyte on the end of a glass rod be taken, as is often recommended, in testing for the end reaction, because it is often the case that no brown appearance is shown by a single drop, yet on taking 1 c.c. of the electrolyte and treating it with sulphuretted hydrogen, distinct traces of nickel can be found in the solution.

As soon as all the nickel has been deposited, wash the cathode several times with distilled water, then with a little alcohol, and dry in the steam oven or over the bunsen flame—this, however, must be done cautiously.

**Removal of Deposit.**—Nickel, when electrolytically deposited, has a great tendency to become “passive;” it is for this reason, as a rule, very difficult to dissolve. Warm nitric or sulphuric acid may be used for dissolving it. Great care must be taken that the whole of the nickel has been dissolved off the cathode before it is again ignited, preparatory to further use. The nickel deposit is at times so bright that it is not easy to tell for certain whether the whole of the deposit has been dissolved or



not; it is very harmful to the platinum electrode to ignite it while there is still a trace of the deposit upon it, as it will be found that black marks are formed upon it which are only removed with great difficulty.

Satisfactory deposits cannot readily be obtained from neutral solutions of nickel containing neutral inorganic salts. Thus, when a solution of a neutral salt of nickel containing sodium or potassium sulphate is subjected to electrolysis, it is only by using a high E.M.F. that it is possible to deposit the nickel; but since, owing to the ready conductivity of a solution of such a salt, a high E.M.F. can only be obtained by employing a relatively high current, or by having the electrodes placed a great distance apart—this solution is not convenient to employ. Neither is a satisfactory deposit obtained when the double cyanide of nickel and potassium is used.

**Organic Salts.**—Very good deposits of nickel can be obtained by using ammonium oxalate or tartrate, but when these organic salts are used there is a tendency for the deposit to be more or less contaminated with carbon; if, however, the C.D. employed is not too high the results are usually quite satisfactory.

**Double Oxalate.**—The solution may be prepared by dissolving the nickel salt in water, and then dissolving 4 to 5 grams of ammonium oxalate in water and adding this solution to that of the nickel salt. It is best to electrolyse at a temperature of from  $45^{\circ}$  to  $50^{\circ}$ . With a current of 1 ampere the separation will be complete in from four to five hours; the E.M.F. will be from 3 to 3.5 volts. When the deposition is conducted at ordinary temperatures, the time required is from  $5\frac{1}{2}$  to  $6\frac{1}{2}$  hours. The deposit may have a brilliant polished appearance or may be matt and greyish.

**Double Tartrate.**—The deposit obtained when a solution containing the double tartrate of ammonia and nickel is electrolysed is generally very brilliant, and the results are quite as trustworthy as when the oxalate is employed. About 3 grams of ammonium tartrate is sufficient, and the C.D. should not exceed 0.9 ampere,

and is better to be 0.4 to 0.6. With a temperature of about 40° the deposition of the metal is complete in four to five hours; the E.M.F. is from 3.8 to 5.5 volts. Exceedingly brilliant deposits are obtained when a current of 0.10 to 0.20 ampere is employed, and the electrolysis conducted over night. Specks of carbon are often noticed when the deposit obtained from organic salts is dissolved in acid, owing to carbon being deposited along with the metal.

**Ammonium Hydrate and Ammonium Borate.**—This solution is made up by dissolving the nickel salt in about 30 c.c. water and then adding about 70 c.c. of a solution consisting of 50 grams of ammonium borate dissolved in 700 c.c. water and 300 c.c. of ammonium hydrate (sp. gr. 0.88). Use a current of 0.5 to 1 ampere, and electrolyse at about 30°. Or the solution may be electrolysed cold with a current of 0.2 to 0.4 of an ampere, and run overnight. Sometimes there is a tendency for a slight anode deposit to be formed; if this is noticed, the addition of a few cubic centimeters of strong ammonia will cause its disappearance. The time required is from three to four hours. This method has been found by the author to be very accurate, but the appearance of the deposit is not so fine as when the other methods are employed, being usually of a dead silver-white colour, which at times has a distinct brownish or smoky tinge.

Although a solution containing sodium phosphate and phosphoric acid gives such very good results in the case of cobalt (p. 98), it is not so satisfactory when employed with nickel, the results being rather low.

#### LITERATURE.

Merrick, *Amer. Chem.*, II. 136; Gibbs, *Zeit. f. Anal. Chem.*, III. 336; *Ibid.*, XI. 10; *Ibid.*, XXII. 558; Wrightson, *Zeit. f. Anal. Chem.*, XV. 300 and 333; Cheney and Richards, *Amer. Jour. of Science and Arts*, XIV. 178; Ohl, *Zeit. f. Anal. Chem.*, XVIII. 523; Luckow, *Zeit. f. Anal. Chem.*, XIX. 314; Riché, *Zeit. f. Anal. Chem.*, XXI.; Classen and Von Reiss, *Ber.*, XIV. 1622 and 2771; Classen, *Ber.*, XXVII. 2061; Vortmann, *Zeit. f. Elektrochem.*, I., 1894, 141; Sucht, *Zeit. f. Anal. Chem.*, XXI. 493; Kohn and Woodgate, *Soc.*

*Chem. Ind.*, VIII. 256; Marshall, *British Assoc. Report*, 1888; Rüdorff, *Zeit. f. Angew. Chem.*, 1892, 6; Brand, *Zeit. f. Anal. Chem.*, XXVIII. 588; Vortmann, *Monatsheft.*, XIV. 536; Campbell and Andrews, *Amer. Chem. Soc.*, XVII. 125; Oettel, *Zeit. f. Elektrochem.*, I. 192; Fresenius and Bergmann, *Zeit. f. Anal. Chem.*, XIX. 320; Cohen and Gläser, *Zeit. f. Anal. Chem.*, 33, 9; Taggart, *Tr. Amer. Chem. Soc.*, 25, 1039; Perkin and Prebble, *Trans. Faraday Society*, 1904.

### Cobalt.

Nickel and cobalt are chemically and physically very much alike in character, and for this reason all chemical methods of separating these metals are beset by considerable difficulties; electrolytically the same difficulties exist. Cobalt is a much more difficult metal to separate from its solutions in the pure state than nickel. Not only are the results almost invariably slightly too high, but generally the appearance of the deposit leaves very much to be desired, being often of a brown to black appearance, and it is only rarely that it can be obtained as a really brilliant deposit.

But, strange as it may appear, it often happens that the deposits which are marked by their unsightly appearance give just as good—if not better—results analytically than those which are bright. The author has made a very careful study of the best electrolytes and conditions for obtaining accurate analytical results and, at the same time, satisfactory deposits of cobalt.

Extremely brilliant deposits may be obtained when sodium hypophosphite is added to the electrolyte, but as a rule the results are about 5 per cent. too high, owing to the deposition, not of pure cobalt, but of a phosphide of cobalt. Fairly correct analytical numbers can be obtained by using ammonium sulphate and ammonia, but the deposit is almost invariably of a dark-brown colour. Of organic salts, ammonium tartrate gives the best deposit, but the results are usually slightly too high. The reason that the electrolytic deposition of cobalt is generally slightly too high is probably due to the fact that cobalt is more readily oxidisable than nickel; and yet this seems strange, because a good

deposit of cobalt retains its brightness in moist air equally as well, if not better than nickel. The most satisfactory results, both analytically and from point of view of the appearance, are obtained with sodium phosphate ( $\text{NaH}_2\text{PO}_4$ ) and phosphoric acid.

**Ammonium Sulphate and Ammonia.**—Make up the solution as described under nickel, except that it is better to add a rather larger quantity of ammonia, from 35 to 40 c.c. (sp. gr. 0.88). In order to obtain the best deposits it is advisable to commence electrolysis with a low current of from 0.3 to 0.4 ampere, and the temperature of the solution should be from 30° to 40°. After the electrolysis has proceeded for about an hour, the C.D. may be increased to 1 ampere. The removal of the last traces of cobalt takes considerably longer than is the case with nickel, the deposition often requiring more than four or five hours, and there is therefore a tendency to obtain rather low numbers, unless the current is passed for a considerable time.

**End Reaction.**—This is found by the same method as that used for nickel, *i.e.* with sulphuretted hydrogen. Or take a few drops of the electrolyte, place in a test tube, make just acid with acetic acid, and add about 2 c.c. of ammonia thiocyanate; then add 2 c.c. amyl alcohol and 1 c.c. ether. On shaking up, if any cobalt remains in solution an intense blue colour is produced in the ether and amyl alcohol layer. This latter test is extremely delicate.

**Removal of Deposit.**—Contrary to the experience with nickel, cobalt deposits are extremely readily removed on the addition of moderately strong nitric acid. The cobalt shows no tendency to assume the passive state.

**Ammonium Tartrate.**—The cobalt is dissolved in a little water and a solution of about 3 grams of ammonium tartrate added to it, after which the mixture is made up to the required volume with distilled water. The pink solution thus obtained is subjected to electrolysis with a commencing current of 0.2 to 0.4 ampere, which is raised after an hour to 1 ampere, or, in cases

where the electrolysis is conducted overnight, the lower current is employed throughout. With the higher current the time required is about four or five hours. The results obtained are usually slightly high, owing to small quantities of carbon being deposited along with the cobalt. The deposited cobalt often has a brilliant burnished appearance, more especially when the electrolysis is carried out with low currents. It may, however, have a smoky and brown surface.

**Ammonium Oxalate.**—The solution is made up in a similar manner to that described for nickel (p. 94). The C.D. should be low at the commencement of the operation, but may be raised to 1.4 ampere after the first fifty minutes. Generally speaking, the deposit has a very poor appearance, but sometimes it is quite bright, as if it had been burnished. The time necessary for the operation varies from 5 to 6½ hours. When a low current is employed and the electrolysis is conducted overnight, it is usually advisable, in order to remove the last traces of cobalt, to raise the current to 1 or 1.3 amperes for half an hour before disconnecting the electrodes. As with the tartrates, so with oxalates, small traces of carbon are usually deposited along with the metal, and the results are thus slightly high.

**Ammonia and Ammonium Borate.**—The cobalt deposits obtained by electrolysing solutions containing borates are not generally very sightly, and the results are usually rather high, but are more accurate than by any of the previous methods described. The solution and the conditions are the same as those described under nickel (p. 95).

**Sodium Phosphate and Phosphoric Acid.**—The solution from which the most exact results can be obtained is one containing sodium di-hydrogen phosphate and a little free phosphoric acid. The solution is made up by adding 2 c.c. of a 5 per cent. solution of phosphoric acid to the cobalt salt, dissolved in 70 to 80 c.c. of water; and then 20 to 25 c.c. of a 10 per cent. solution of di-hydrogen sodium phosphate is run in from a burette.

The solution should be stirred with a glass rod during the addition of the sodium phosphate, to prevent the formation of the double salt of cobalt and sodium phosphate. The solution is then made up to the required bulk, and electrolysed.

It is important to use *di-hydrogen sodium phosphate* or the corresponding ammonium or potassium salt, because if  $\text{Na}_2\text{HPO}_4$  or  $\text{Na}_3\text{PO}_4$  are employed, the double salt of sodium and cobalt phosphate precipitates out as an almost insoluble purple powder, and it requires the addition of large quantities of phosphoric acid to bring it into solution again. It might be supposed that equally satisfactory results would be obtained by adding a large quantity of phosphoric acid in the first case, but as it is very difficult to gauge the right quantity of phosphoric acid which it is necessary to add, this is not to be recommended.

The electrolysis should be commenced cold with a low C.D. of 0.2 to 0.3 ampere; after about an hour the current may be raised to 0.8 to 1.2 ampere, and the solution warmed to from  $50^\circ$  to  $60^\circ$ . It often happens that when the electrolysis has proceeded for some thirty or forty minutes a brown anode deposit is obtained; this is especially the case when the electrolysis is commenced hot, the deposit being in this case sometimes quite black. It will be found that the addition of 0.1 to 0.2 gm. of hydroxylamine sulphate or chloride causes the almost immediate disappearance of the anode deposit. If, after being removed, the deposit returns again, a further addition of the hydroxylamine salt may be made. Formaldehyde can also be used to remove the anode deposit, but it acts very much more slowly. The following conditions will be found to give satisfactory results—

C.D. . . . .	0.2 increasing to 1.2 ampere.
E.M.F. . . . .	2.0 to 3.5 volts.
Temp. . . . .	cold at commencement, but may be raised to $50$ or $60^\circ$ after about an hour.
Time : . . . .	4 to 6 hours.

The deposit is almost invariably brilliant, being very rarely marred by burning. It is an advantage, after the solution has become colourless, to add a few drops of very dilute ammonia to

neutralise the excess of acid which has been formed during the electrolysis. The neutralisation of the acid causes the last traces of cobalt—which are always rather difficult to precipitate—to be deposited much more rapidly.

This method gives a better deposit and more accurate results than any other process at present in use.

#### LITERATURE.

Gibbs, *Zeit. f. Anal. Chem.*, III. 336; *Ibid.*, XI. 10; *Ibid.*, XXII. 548; Wrightson, *Zeit. f. Anal. Chem.*, XV. 300 and 333; Schweder, *Zeit. f. Anal. Chem.*, XVI. 344; Ohl, *Zeit. f. Anal. Chem.*, XVIII. 523; Luckow, *Zeit. f. Anal. Chem.*, XIX. 314; Riché, *Zeit. f. Anal. Chem.*, 116; Schucht, *Zeit. f. Anal. Chem.*, XXI. 493; Brand, *Zeit. f. Anal. Chem.*, XXVIII. 588; Cheney and Richards, *Amer. Journ. of Science and Arts*, XIV. (3), 178; Classen and Von Reiss, *Ber.*, XIV. 1622 and 2771; Classen, *Ber.*, XXVII. 2061; Le Roy, *Compt. Rendus*, CXII. 722; Vortmann, *Monatsheft.*, XIV. 536; Kohn and Woodgate, *Journ. Soc. Chem. Ind.*, VIII. 256; Marshall, *British Assoc. Report*, 1898, 300; Oettel, *Zeit. f. Elektrochem.*, I. 195; Fresenius and Bergmann, *Zeit. f. Anal. Chem.*, XIX. 329; Perkin and Prebble, *Trans. Faraday Soc.*, 1904.

#### Iron.

Owing to the fact that, on electrolysing neutral solutions of iron salts of inorganic acids, ferric hydrate is always precipitated at the anode, and that it is not possible to deposit iron quantitatively from solutions acidified with mineral acids, it is only possible to obtain deposits of iron, which are satisfactory from an analytical point of view, by using salts of organic acids in the electrolyte. It is a well-known fact that the presence of most organic acids prevents the precipitation of iron from its salts as hydrate by means of ammonia, and this fact is sometimes made use of in ordinary qualitative analysis to separate the iron from such metals as cerium, for example. But among organic acids or salts of organic acids, there are very few which can satisfactorily be employed as electrolytes in the electrolytic analysis of iron; the reason being that, with organic acids of higher molecular weight,

the iron deposit invariably contains traces of carbon, which at times are so considerable as to cause really serious errors. Furthermore, practically only salts of ammonia may be employed; salts of sodium or potassium cannot be used because, as the organic acid is decomposed, carbonates of these metals are produced, and this causes precipitation of hydrated carbonate of iron. But whatever organic acid is employed, even with oxalates and tartrates, carbon is invariably deposited to a more or less extent with iron. Further, the higher the current density, the greater the tendency for deposition of carbon to take place. As a matter of fact, the small traces of carbon deposited along with the iron, when the ammonium salts of oxalic and tartaric acid are employed, do not seriously interfere with the value of the process, because it is extremely difficult, if not impossible, to throw out the last traces of iron which remain in the solution, and it is found that the slight error due to the deposition of carbon, along with the iron, is practically counterbalanced by the small traces of iron which remain in the solution. There is, however, some diversity of opinion upon this subject; Classen, for example, considers that if the current is kept below 1 ampere, carbon is not deposited; other authorities, however, are unable to agree with Classen upon this point.

**Ammonium Oxalate.**—This method, which was first suggested by Classen, is the one generally recommended for analysis of iron. The iron solution, which should be free from chlorides or nitrates, must be poured into the solution of ammonium oxalate, if it is in the ferrous condition; otherwise, if the solution of ammonium oxalate is added to the solution of the ferrous salt, a precipitate of ferrous oxalate is produced, which can only be dissolved again with considerable difficulty, if, indeed, it is possible to dissolve it at all. With ferric salts, it does not matter whether the oxalate is added to the iron salt or the iron salt to the oxalate.

Dissolve 5 to 7 gm. of ammonium oxalate or acid ammonium oxalate in a small quantity of hot water, and add the iron salt.



ferrous ammonium sulphate—also dissolved in a little water, and make the solution up to about 150 c.c. As the electrolysis proceeds it will sometimes be noticed that a small quantity of ferric hydrate separates out in the form of a flaky precipitate; if this takes place it is necessary to add small quantities of oxalic acid to dissolve the precipitate. The formation of this precipitate, which is due to the solution becoming alkaline as the electrolysis proceeds, is the chief objection to the oxalate method, because more attention is required than in the case of the tartrate, in which this does not occur. According to Smith and Muir,<sup>1</sup> the addition of 5 c.c. of a saturated solution of borax is an advantage, extremely good results being obtained when this substance is present.

## CONDITIONS.

I.		II.	
C.D.	. . . 0.6 to 1.2 ampere.	C.D.	. . . 0.6 to 1 ampere.
E.M.F.	. . . 4 to 4.3 volts.	E.M.F.	. . . 3.7 to 4.3 volts.
Temp.	. . . normal.	Temp.	. . . 50° to 60°.
Time.	. . . 4 to 5 hours.	Time	. . . 2.5 to 3.5 hours.

**End Reaction.**—Withdraw at least 1 c.c. of the solution from the electrolyte, acidify with hydrochloric acid, and add at least two or three cubic centimeters of a solution of potassium thiocyanate. As long as a red coloration is produced it is necessary to continue the electrolysis.

The deposited iron has generally the appearance of polished steel, but at times it has a rather foggy look, or may have brownish streaks. As soon as the electrolysis is finished, the deposit is washed, *as rapidly as possible*, with distilled water, and then with absolute alcohol, and dried either in the steam oven or by carefully holding above the Bunsen flame. If it is not dried fairly rapidly, the results may be too high, owing to slight superficial rusting. Dilute sulphuric acid is the best solvent. When the deposit is dissolved, minute specks of carbon may be noticed in the solution, and the hydrogen given off usually has that

<sup>1</sup> *Amer. Chem. Soc.*, 18, 654.

peculiar smell which is produced when metals containing carbon are dissolved in acids.

**Ammonium Tartrate.**—Dissolve 3 to 4 gm. of ammonium tartrate in water, and add the iron salt to the solution; or the solution of ammonium tartrate may be added to the iron solution. The yellow solution thus obtained is electrolysed with a C.D. of 1 to 1.3 amperes, the E.M.F. being about 4.7 to 6 volts. One advantage in using the tartrate solution is that there is never precipitation of ferric hydrate, as is often the case when ammonium oxalate is employed; therefore the process requires less attention. It will be found, as in the case of oxalates, that the metallic deposit always contains traces of carbon; therefore the tendency is for the results to be fractionally too high. But according to a long series of experiments carried out by the author, if the C.D. is not allowed to rise too high, this is negligible. With currents of from 0.8 to 1.1 ampere, the time required for complete deposition is from  $2\frac{3}{4}$  to 4 hours. When the electrolysis is carried out overnight, a current of 0.25 to 0.4 ampere is sufficient.

It will be found that the iron from ferric salts takes an appreciably longer time to deposit than the iron from ferrous salts.

### **Electrolysis of Iron Salts containing an Organic Radical.**

Many pharmaceutical preparations of iron contain the iron united with an organic acid. Since the presence of the organic radical prevents the precipitation of the iron on the addition of ammonium hydrate, the analysis of these substances by ordinary chemical methods is rather troublesome. These iron salts can often be directly analysed electrolytically by dissolving them in water and adding 4 or 5 gm. of ammonium tartrate, making up to the required bulk and electrolysing.

Generally speaking, the deposition is rather more protracted than when iron salts with an inorganic radical are analysed, but

the excess of time is not very great except with iron salts of citric acid, in which case it is often very tedious.

#### LITERATURE.

Wrightson, *Zeit. f. Anal. Chem.*, XV. 305; Luckow, *Zeit. f. Anal. Chem.*, XIX. 18; Classen and Von Reiss, *Ber.*, XIV. 1622; Classen, *Zeit. f. Elektrochem.*, I. 288; Smith, *Amer. Chem. Journ.*, X. 330; Moore, *Chem. News*, LIII. 209; Brand, *Zeit. f. Anal. Chem.*, XXVIII. 581; Rüdorff, *Zeit. f. Angew. Chem.*, XV. 198; Vortmann, *Monatsh.*, XIV. 542; Heidenreich, *Ber.*, XXIX. 1585; Kohn, *British Assoc. Report*, 1896; Avery and Dales, *Ber.*, 32, 64; Verwer and Goll, *Ber.*, 32, 806; Avery and Dales, *Ber.*, 32, 2233.

### Mercury.

Ordinary chemical methods of analysing mercury are rather tiresome, but it is very readily separated from its solutions by means of the electric current. Further, it adheres tenaciously to platinum, especially if it has been sand-blasted, and is therefore readily weighed. A gauze flag electrode is best suited for determinations of mercury, because very considerable quantities of mercury will adhere to it, without falling off. The author has also obtained very satisfactory results with a gold cathode containing 5 per cent. of platinum to stiffen it. The mercury adheres very firmly, producing an amalgam. It is, however, readily removed by heating the electrode in the Bunsen flame. See Note, p. 284.

The solutions from which the metal may be deposited are those containing nitric or sulphuric acid; hydrochloric acid can also be employed, and very satisfactory results may be obtained from solutions in sodium sulphide or in potassium cyanide.

**Sulphuric Acid.**—The mercury salt is dissolved in water, and from 1 to 2 c.c. of concentrated sulphuric acid added for every 100 c.c. of solution. The electrolysis is conducted with a C.D. of from 0.3 to 0.8 ampere; towards the end of the operation the current may be increased to 1 ampere. The potential difference is from 3.3 to 3.6 volts. The operation can be carried out at ordinary temperatures, but it is more rapid when a temperature

of from  $50^{\circ}$  to  $60^{\circ}$  is employed. During the electrolysis mercurous salts are often produced owing to cathodic reduction, and are precipitated. As a rule, however, this causes no trouble, as they gradually pass into solution, and are then deposited out as metallic mercury. The addition of a few drops of hydrochloric acid causes their more rapid disappearance. As a matter of fact, mercurous salts can be directly employed; in this case they are suspended in water with the requisite quantity of sulphuric acid (see above), a few drops of hydrochloric acid added, and the current passed. Even such insoluble compounds as cinnabar can be analysed in this way. The most satisfactory method of getting rid of the mercurous salts is to add a small quantity of ammonium or potassium persulphate. The persulphate gradually oxidises the mercurous salt to the mercuric condition. It is not advisable to add large quantities of the persulphate at one time; about 0.1 grm. should be added from time to time. The formation of the mercurous salt can be entirely prevented by adding the persulphate at the commencement of the electrolysis.

**End Reaction.**—In order to ascertain whether all the mercury has been deposited, about 1 c.c. of the solution is drawn off, and a little sulphuretted hydrogen water added; if the solution becomes brownish, this shows that all the mercury has not been deposited. Or a small piece of thin copper wire may be hung over the cathode, so that it just dips in the liquid; if, after ten minutes, there is no deposit of mercury on the copper wire, the electrolysis may be considered at an end.

**Washing the Deposit.**—The mercury adheres firmly to the cathode in the form of minute globules. As soon as the process is finished, the cathode is washed several times with water and dried in a desiccator. The use of alcohol is not permissible, as it loosens the globules and also coats the mercury with a thin, greyish pellicle. When, however, a gold cathode is employed, there is no objection to washing with water, and then with alcohol, because the mercury is amalgamated with the surface of the cathode. As drying in a desiccator takes some hours, it is

therefore recommended to use a gold flag electrode, made of sheet gold; because, after washing with absolute alcohol, the electrode can be dried in a few minutes by means of an air blast. It should, however, after the alcohol has been driven off, be placed in a desiccator for half an hour before weighing. The mercury is readily removed from the gold electrode, by heating it to low redness in the flame of a Bunsen burner.

**Nitric Acid.**—Add from 2 to 3 c.c. of concentrated nitric acid to every 100 c.c. of solution, and electrolyse at a temperature of about  $50^{\circ}$ . The time required for about 0.5 gm. of mercuric chloride is from 4 to 5 hours.

#### CONDITIONS.

C.D. . . . .	0.1 to 0.2 ampere.
E.M.F. . . . .	2 to 2.3 volts.

Owing to the presence of nitric acid the end reaction in this case is best ascertained by neutralising with ammonium, and adding a few drops of hydrochloric acid and then sulphuretted hydrogen.

**Hydrochloric Acid.**—When hydrochloric acid is employed as the electrolyte, only a small quantity should be used, not more than 1 c.c. to the 100 c.c. of solution. The current conditions are the same as those described for sulphuric acid. Several other methods have been suggested for the electrolysis of mercury solutions. Classen, for example, uses ammonium oxalate; Edgar F. Smith obtains good results from a solution containing potassium cyanide, and also from solutions containing sodium sulphide.

**Sodium Sulphide.**—From 20 to 25 c.c. of sodium sulphide, prepared as described on p. 281, is added to the mercury solution, which is then made up to 125 to 150 c.c., and electrolysed under the following conditions:—

C.D. . . . .	0.11 to 0.15 ampere.
E.M.F. . . . .	2.5 to 2.7 volts.
Temp. . . . .	$65^{\circ}$ to $70^{\circ}$
Time . . . . .	4 to 5 hours.

If the mercury salt is contained in an acid solution, the mercury can be precipitated as sulphide by passing hydrogen sulphide into

it, which, after filtering off and washing, may be dissolved in 20 to 25 c.c. of sodium sulphide solution.

The deposit of mercury obtained is bright and adherent. E. Smith has employed this method for the direct analysis of cinnabar. The finely powdered cinnabar is placed upon the bottom of a weighed platinum basin, which is made the anode, and the mercury deposited upon a platinum spiral, which should, for this purpose, be sand-blasted. The estimation, according to Smith, employing the conditions set out above, does not exceed 3 hours.

**Potassium Cyanide.**—From 1 to 1.5 grm. potassium cyanide is used for every 0.1 to 0.2 grm. of metallic mercury.

#### CONDITIONS.

C.D. . . . .	0.02 to 0.10 ampere.
E.M.F. . . . .	1.6 to 3.4 volts.
Temp. . . . .	65°
Time . . . . .	3 to 4 hours.

The metal when deposited from this solution coats the electrode evenly, and has a greyish appearance.

### Estimation of Mercury in Pharmaceutical Preparations.

It sometimes happens that the estimation of mercury in pharmaceutical preparations, especially substances containing an organic radical, is a matter of considerable difficulty; electrolytically, however, there is no difficulty in the estimation.

It will depend upon circumstances which of the methods described will be found the most convenient to employ. Mercury tannate, for example, dissolves readily in sodium sulphide; it can, therefore, be readily deposited from this solution. Lister's cyanide may be estimated from cyanide solutions. Mercury salicylate, and other organic substances which do not readily dissolve in either of these solvents, are best determined from solutions containing nitric or sulphuric acid.

When nitric acid is employed, the substance should be covered with a little fuming nitric acid, and heated until most of the organic material has been oxidised. The product is then diluted with

water, and electrolysed as usual. When sulphuric acid is used, the substance is covered with concentrated sulphuric acid, about 1 grm. of ammonium or potassium persulphate, and the mixture heated until the, at first, black mass becomes nearly colourless; it is then diluted with water, filtered if necessary, and electrolysed as described on p. 104.

NOTE.—When a basin electrode is used as cathode for the analysis of mercury, there is a tendency for the results to be too low, more especially when the temperature of the bath rises above  $50^{\circ}$ —the electrolysis is often conducted at  $70^{\circ}$ ;—Bindschedler has shown that this is due to the evaporation of the solution, and the consequent exposure of the already deposited metal to the atmosphere. With the flag electrode, which dips completely below the surface of the solution, this difficulty does not arise.

#### LITERATURE.

Classen and Ludwig, *Ber.*, **10**, 323; Hoskinson, *Amer. Chem. Journ.*, **8**, 209; Smith and Kerr, *Amer. Chem. Journ.*, **8**, 206; Smith and Frankel, *Amer. Chem. Journ.*, **11**, 264; Vortmann, *Ber.*, **24**, 2749; Brandt, *Zeit. f. Anorg. Chem.*, **1891**, 202; Riidorff, *Zeit. f. Anorg. Chem.*, **1892**, 5; Schmucker, *Journ. Amer. Chem. Soc.*, **15**, 204; Rising and Lenher, *Berg. und Hütten Zeit.*, **55**, 175; Wallace and Smith, *Journ. Amer. Chem. Soc.*, **18**, 169; Fernberger and Smith, *Journ. Amer. Chem. Soc.*, **21**, 1006; Kollock, *Journ. Amer. Chem. Soc.*, **21**, 911; Bindschedler: *Zeit. f. Elektrochem.*, **8**, 329; Medicus and Mebold, *Zeit. f. Elektrochem.*, **8**, 690.

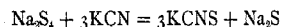
### Antimony.

One of the most important properties of antimony is its power to form complex anions. It forms, in fact, two monovalent anions, antimonious ( $\text{SbO}_2$ ) and antimonic ( $\text{SbO}_3$ ). It further has the power of forming thio-salts, in which the oxygen is replaced by sulphur; we have thus thio-antimonious anions ( $\text{SbS}_2$ ) and thio-antimonic anions ( $\text{SbS}_3$ ). From the point of electro-chemical analysis the salts of these of anions are of the greatest importance, because it is from them that we obtain the most satisfactory deposits of antimony. As a matter of fact, antimony can be precipitated from acid solutions<sup>1</sup>

<sup>1</sup> From hydrochloric acid solutions an explosive variety of antimony is obtained, which, according to Gore, contains about 6 per cent. of trichloride.

and from solutions containing potassium oxalate, but the deposits do not adhere firmly or satisfactorily to the cathode. Tartrates may also be employed, and satisfactory quantitative results can be obtained from neutral tartrate solutions, which are electrolysed at high temperatures.

Ammonium sulphide or sodium sulphide may be employed, preferably the latter, because, when ammonium sulphide is used, especially if it contains polysulphides, there is usually a certain quantity of sulphur deposited upon the precipitated metal. It is a rather difficult matter to remove this sulphur, which generally forms a thin and homogeneous skin over the metallic deposit. But after washing with alcohol, the sulphur can be removed by carefully rubbing with a piece of rubber-tubing fastened on to the end of a piece of glass rod. Of course another objection to the use of ammonium sulphide is its unpleasant smell, and its action upon the metallic instruments in the laboratory. Sodium sulphide, which was first suggested by Classen, is not open to the above objections, and gives very good results; it has the additional advantage that, when present in excess, it prevents the deposition of tin. The sodium sulphide ( $\text{Na}_2\text{S}$ ) used must be pure; the method of preparation will be found on p. 281. A. Fischer and also A. Hollard recommend the addition of potassium cyanide to the sodium sulphide solutions, as this prevents the formation of polysulphides, and consequently the deposition of sulphur. The action of the potassium cyanide upon the polysulphides is to form potassium thio-cyanate thus—



The sodium sulphide<sup>1</sup> may be added in excess to the solution of the antimony salt, so long as this is not acid; but it is preferable to acidify with dilute hydrochloric acid, and saturate the solution with sulphuretted hydrogen. The precipitated antimony sulphide is then filtered and washed with hot water, and can be directly dissolved off the filter-paper by pouring on sodium sulphide.

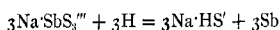
<sup>1</sup> Potassium sulphide is not permissible, because complete deposition does not take place from its solution.



Gauze or roughened electrodes should be used for antimony deposits, because the metal does not adhere well to polished surfaces, and therefore such surfaces can only be used when the amount of antimony is very small.

70 to 80 c.c. of the solution of sodium monosulphide, prepared as described on p. 281, is used for dissolving the sulphide, or is added to the antimony solution. It is best to electrolyse at a temperature of  $50^{\circ}$  to  $60^{\circ}$ , with a current of from 0.8 to 1 ampere; the E.M.F. is between 1.3 to 2.5 volts. Under these conditions the time required is from  $2\frac{1}{2}$  to  $3\frac{1}{2}$  hours. When a cold solution is electrolysed with a current of from 0.2 to 0.4 ampere, the time required for complete deposition is from 17 to 18 hours.

The reaction may be represented as one of reduction of the anion  $\text{SbS}_3'''$ .



When antimony is obtained in solution with polysulphides, as, for example, in analysis, the excess of sulphur which is then present would make the solution unsuitable for electrolytic determinations. Classen recommends heating the solution with an excess of ammoniacal hydrogen peroxide until it becomes colourless. It may happen, if too large an excess of the peroxide has been added, that, owing to the decomposition of the alkali sulphide, antimony sulphide is precipitated. As soon as the solution is colourless, or if sulphide of antimony has been precipitated, about 70 c.c. of the solution of sodium sulphide is added. Or, instead of using hydrogen peroxide, a solution of potassium cyanide may be added until the yellow solution becomes colourless.

**End Reaction.**—The end of the electrolysis can be told by hanging a small piece of platinum wire over the cathode for about ten minutes; if there is no deposit, this shows that all the antimony has been thrown out. Or 1 c.c. of the solution may be withdrawn, and acidified with hydrochloric acid. An orange precipitate or coloration shows that the process must be continued.

If ammonium sulphide is used instead of sodium sulphide, it

is best to employ the hydrosulphide  $\text{NH}_4\text{HS}$ , as there is less likelihood of sulphur being deposited at the cathode, although as a rule a certain amount is deposited on the anode.

**Removal of the Deposit.**—The antimony can be dissolved off the cathode by means of a mixture of nitric and tartaric acids. When tartaric acid is not used, antimony oxide is formed, and this is sometimes rather difficult to remove.

**Deposition from Sulphide Solutions containing Potassium Cyanide.**—The antimony salt or sulphide is treated with 60 or 80 c.c. of sodium sulphide, as already described, and from 20 to 30 c.c. of a freshly prepared solution of potassium cyanide run into the solution; if this quantity is not sufficient to cause the solution to become colourless, more must be added until the solution is no longer coloured.

#### CONDITIONS.

C.D. . . . .	0.3 to 0.8 ampere.
E.M.F. . . . .	1.7 to 1.9 volts.
Temp. . . . .	20° to 30°
Time . . . . .	5 to 6 hours.

With currents of 0.1 to 0.2 ampere and in a cold solution, the time required is about 18 hours.

**From Tartrate Solutions.**—As is well known, antimony compounds readily dissolve in tartaric acid or tartrates. The deposition of antimony from solutions in free tartaric acid is very slow, and the E.M.F. required is high owing to the small amount of ionisation of tartaric acid. On the other hand, the whole of the antimony can be deposited in  $2\frac{1}{2}$  to 3 hours, when a neutral solution of ammonium tartrate is employed. When deposited from cold solutions, the metal is rather amorphous in character, but with care it may be washed and dried. When deposited with low currents and at high temperatures, the metal adheres very firmly and is often quite brilliant. The solution is prepared by dissolving the antimony salt in water, and adding 8 to 10 gm. of ammonium tartrate; or it is dissolved in tartaric acid, and the solution then neutralised with ammonia.

## CONDITIONS.

I.		II.	
C.D. . . .	0.25 to 0.5 ampere.	C.D. . . .	0.2 ampere.
E.M.F. . .	3 volts.	E.M.F. . .	2.5 volts.
Temp. . . .	70° to 80°	Temp. . . .	ordinary temperature.
Time . . . .	2½ to 3 hours.	Time . . . .	all night.

## LITERATURE.

Parodi and Mascazzini, *Zeit. f. Anal. Chem.*, XVIII. 588; Luckow, *Zeit. f. Anal. Chem.*, XIX. 13; Classen and Von Reiss, *Ber.*, XIV. 1622; *Ibid.*, XIV. 1622; *Ibid.*, XVII. 2467; *Ibid.*, XVIII. 1104; Brand, *Chem. Zeit.*, 1889, 1219; Vortmann, *Ber.*, XXIV. 2762; Kohn, *British Assoc. Report*, 1896, 251; Rüdorff, *Zeit. f. Angew. Chem.*, 1892, 199; Classen, *Ber.*, XXVII. 2060; Fischer, *Ber.*, 38, 2348; Hollard, *Bull. Soc. Chim.*, 29, 262.

## Tin.

Tin, like antimony and arsenic, forms oxides which have an acidic character, and, like these elements also, has the power of forming thio-salts. The capacity for giving thio-salts is linked with the capacity of these metals to form acid oxides. Just as these oxides dissolve in alkalis, so the sulphides dissolve in alkaline sulphides. As is the case with antimony, so one of the most satisfactory methods for depositing tin is from the thio-salts; in this case, however, not, as with antimony, from the sodium salt, but from its ammonium salt. In weak solutions of sodium sulphide, tin is only partly precipitated, while in strong solutions it is not thrown out at all. Hence we have here a method for the separation of tin and antimony. See p. 181.

**Deposition from Ammonium Sulphide.**—Sufficient yellow ammonium sulphide to dissolve the precipitate first formed is added to the solution of the tin salt. If the solution is acid it must first be neutralised with ammonia; and if in doing this a slight precipitate is caused, it may be neglected, because the action of the ammonium sulphide will dissolve it. The solution is then made up to the required volume with distilled water, and electrolysed at a temperature of 50° to 60°. The current density

may be from 1 to 1.8 amperes, and the E.M.F. will be from 3.5 to 4.5 volts. With these conditions the time required is from  $3\frac{1}{2}$  to  $4\frac{1}{2}$  hours. If sulphur is deposited upon the cathode it can, after washing with alcohol, be removed by gentle rubbing with a piece of rubber fixed on the end of a glass rod.

When, as is sometimes the case in analysis, the tin is already in solution with sodium sulphide, it is necessary to convert it into the ammonium salt before electrolysing it. To do this, Classen recommends the addition of from 20 to 25 gm. of *pure* ammonium sulphate to the solution, which is then gently warmed until no more sulphuretted hydrogen is evolved; it is then kept gently boiling for another 10 or 15 minutes. When the conversion into ammonium sulphide is complete, the solution becomes greenish yellow. If the mixture is heated too long, tin sulphate or hydrate may separate out, in which case it is dissolved in ammonium sulphide. If, after cooling, any sodium sulphate should crystallise out, it is dissolved by the addition of water.

**End Reaction.**—Withdraw about 1 c.c. of the solution, acidify with dilute sulphuric acid, and gently warm. If the solution deposits brown or yellow stannous or stannic sulphide, the electrolysis must be continued. A small quantity of sulphur will, of course, be precipitated, because of the decomposition of the ammonium sulphide.

**Double Oxalate.**—According to Classen, satisfactory deposits of tin can be obtained by electrolysing a solution containing ammonium oxalate and oxalic acid. But unless oxalic acid is present in excess, flakes of tin hydroxide are precipitated, owing to the solution becoming alkaline from the decomposition of the ammonium oxalate. In preparing the oxalate solution, 4 gm. ammonium oxalate should be employed for every 0.3 gm. of tin present, and 9 to 10 gm. of oxalic acid. The solution is electrolysed at a temperature of from 50° to 60°, with a current of 1 to 1.5 amperes. The electrolyte may be kept acid with acetic instead of with oxalic acid. When acetic acid is used, the appearance of the deposit is usually better than when oxalic acid is employed;

it is also to be recommended because it is not decomposed by the electric current, whereas oxalic acid is.

**Removal of the Deposit.**—Tin adheres very firmly to the electrodes, and does not readily dissolve in acids; it is therefore sometimes recommended to first coat the electrodes with copper or silver. In order to remove the deposit, the electrode must be boiled with strong hydrochloric acid, but even then it is only very slowly dissolved. Nitric acid can also be employed, but the surface becomes coated with oxide, which requires to be removed in order that the acid may attack fresh surfaces. Another method is to cover the tin deposit with dilute sulphuric acid and make the electrode the anode, a piece of copper wire serving as cathode.

For purposes of electrolysis, half a gram of tin can be dissolved in hypochloric acid; but this is rather a tedious operation. It is better to use tin ammonium chloride,  $\text{SnCl}_4, 2\text{NH}_4\text{Cl}$ .

#### LITERATURE.

Classen and Von Reiss, *Ber.*, XIV. 1622; Luckow, *Zeit. f. Anal. Chem.*, XIX. 13; Classen, *Ber.*, XVII. 2467; and XVIII. 1104; Bongartz and Classen, *Ber.*, XXI. 2900; Gibbs, *Chem. News*, XL. 291; Rüdorff, *Zeit. f. Angew. Chem.*, 1892, 196; Classen, *Ber.*, XXVII. 2074; Engels, *Zeit. f. Elektrochem.*, II. 417; Freudenberg, *Zeit. f. Phys. Chem.*, XII. 121; Kohn, *Brit. Assoc. Report*, 1896; Campbell and Champion, *Fourn. Amer. Chem. Soc.*, 20, 687.

### Cadmium.

Cadmium cannot be deposited from solutions which contain much free mineral acid, although the presence of a very small quantity is advantageous, as it prevents the deposited metal coming down in the spongy condition. Good deposits can rarely be obtained from neutral or alkaline solutions, the cadmium generally coming down spongy, and is consequently non-adherent. In order to obtain satisfactory deposits of cadmium, it is important

that the C.D. should be equal at all parts of the electrode. There are three methods which may be used for the electrolysis: (1) cyanide, (2) feebly acid solutions, (3) oxalate or tartrate.

**Cyanide Solution.**—About 0.5 gm. of the cadmium salt, preferably the sulphate or acetate, is dissolved in water, and a solution of potassium cyanide added until the precipitate first formed is redissolved; a fair excess of cyanide is an advantage, and causes the deposit to be firmer. The solution is then made up to the required bulk, and electrolysed.

## CONDITIONS.

I.		II.	
C.D.	0.50 to 0.75 ampere.	C.D.	0.1 to 0.3 ampere.
E.M.F.	4.6	E.M.F.	3.3 to 4.5 volts.
Temp.	normal.	Temp.	50° to 60°
Time	6 to 8 hours.	Time	5 to 6 hours.

**End Reaction.**—Add a little sulphuretted hydrogen water to a portion of the solution. If no yellow precipitate or coloration is produced, then the whole of the metal has been deposited.

**Acid Solutions.**—Occasionally very good adherent deposits can be obtained from solutions containing a little free sulphuric acid. The cadmium salt and about 3 gm. of ammonium sulphate is dissolved in water, and from 1 to 2 c.c. of 20-per-cent. sulphuric acid added.

## CONDITIONS.

C.D.	0.1 to 0.3 ampere.
E.M.F.	2.5 volts.
Temp.	60° to 70°
Time	3 to 4 hours.

The deposited metal, when not spongy, is of a brilliant silver-white colour. Instead of using sulphuric acid, the solution may be acidified with acetic or formic acids, in which case the salt of the acid employed is used, instead of ammonium sulphate.

**Oxalate and Tartrate.**—To the solution of the cadmium

salt add a solution of from 8 to 10 grm. of ammonium oxalate. The electrolysis may either be conducted at ordinary or at higher temperatures. It will be found advantageous to add a little oxalic acid from time to time, in order to keep the solution feebly acid. The deposit is then denser and more adherent.

## CONDITIONS.

I.		II.	
C.D.	0.5 to 0.75 ampere.	C.D.	0.5 to 1.0 ampere.
E.M.F.	2.5 to 3.5 volts.	E.M.F.	2.5 to 4.0 volts.
Temp.	50° to 60°	Temp.	normal.
Time	3.5 to 4 hours.	Time	4 to 5 hours.

When tartrates are employed, about 5 grm. of ammonium tartrate and a few drops of tartaric acid are added to the solution. The electrolysis is best conducted at a temperature of from 50° to 60°.

## LITERATURE.

Smith, *Amer. Phil. Soc.*, 1878; Clarke, *Zeit. f. Anal. Chem.*, XVIII. 104; Beilstein and Jawein, *Ber.*, XII. 759; Smith, *Amer. Chem. Journ.*, II. 43; Luckow, *Zeit. f. Anal. Chem.*, XIX. 16; Wrightson, *Zeit. f. Anal. Chem.*, XV. 303; Classen and Von Reiss, *Ber.*, XIV. 1628; Warwick, *Zeit. f. Anorg. Chem.*, I. 258; Moore, *Chem. News*, LIII. 209; Smith, *Amer. Chem. Journ.*, XII. 329; Vortmann, *Ber.*, XXIV. 2749; Classen, *Ber.*, XXVII. 2060; Heidenreich, *Ber.*, XXIX. 1586; Avery and Dales, *Amer. Chem. Soc.*, XIX. 380; Wallace and Smith, *Amer. Chem. Soc.*, XIX. 870, and XX. 279; Balachowsky, *Compt. Rendus*, 131, 384; Miller and Page, *Zeit. f. Anorg. Chem.*, XXVIII. 233; Kollock, *Amer. Chem. Soc.*, XXI. 911; Hollard, *Electro-chemist*, 1904, III. 409.

## Bismuth.

Bismuth is one of the more difficult metals to deposit, electrolytically. In fact, it is a very difficult matter to obtain satisfactory results at all. From a great many solutions the bismuth deposits partly as oxide at the anode, and partly as metal on the cathode. Even when no oxide is deposited, the bismuth is often powdery and spongy, and consequently non-adherent.

Dmitry-Balachowsky<sup>1</sup> gives the following conditions for depositing bismuth :—

- (1) Weakly acid solution.
- (2) Only small traces of the halogens should be present.
- (3) Low current density.
- (4) Roughened electrode.
- (5) Addition of urea or aldehyde.

When the C.D. is too high, oxidation of the deposit takes place.

Balachowsky uses a solution containing free nitric acid: from 0.6 to 1.1 gm.  $\text{Bi}(\text{SO}_4)_3$  is dissolved in water with 5 to 7 c.c. nitric acid, and 3 to 5 gm. urea. The C.D. employed is from 0.04 to 0.06 ampere per square decimeter. E.M.F., 1.7 to 2 volts. Temperature of solution, 60° to 70°. Time, eight to ten hours. Instead of using urea, formaldehyde may be equally well employed.

Wimmenaneur<sup>2</sup> recommends for the solution of the bismuth nitrate a mixture of two parts water and one part glycerol. He also advises the use of a rotating anode, as this prevents the formation of peroxide. The solution is acidified with nitric acid. C.D. 0.1 at the commencement, which is later on reduced to 0.05. The temperature should not be above 50°.

Dr. Kohn<sup>3</sup> found the results irregular when free nitric acid only is present, and obtained better results with sulphuric acid. He states that the best results are obtained when metaphosphoric or citric acid are used. When citric acid is employed the bismuth can be deposited in ammoniacal solutions. The quantity of bismuth present should not exceed 0.2 gm. The commencing C.D. should be 0.08, finishing at 0.2 ampere, the quantity of citric acid taken being 2 to 2.5 gm. The deposition required from eighteen to twenty hours. It is best to precipitate the bismuth as hydroxide, dissolve in sufficient nitric acid, add the citric acid, and then electrolyse.

Although by taking great care good deposits of bismuth can be obtained, generally speaking the results are anything but satisfactory.

<sup>1</sup> *Compt. Rendus*, **131**, 179-182.

<sup>2</sup> *Zeit. f. Anorg. Chem.*, **27**, 1-21.

<sup>3</sup> *British Assoc. Report*, **1900**, p. 173.



## **Zinc.**

Like cadmium, zinc cannot be deposited from solutions which contain more than the merest trace of free mineral acid. Zinc is also very prone to be deposited in a spongy and non-adherent form; this is especially the case with solutions which are quite neutral.

**Deposition of the Metal.**—Electro-deposited zinc, being very pure, is only removed from the electrodes upon which it has been deposited with considerable difficulty. If platinum electrodes are employed, it is advisable to first coat them with a thin layer of copper; because, when zinc is directly deposited upon platinum, as a rule a black powdery coating is left, after the zinc has been dissolved off. This deposit can only be got rid of by rubbing the electrode with fine sand, a proceeding not to be recommended. Vortmann considers that this black deposit consists of finely divided platinum. Instead of using coated platinum electrodes, nickel electrodes can be employed. When nickel is used, it is understood, of course, that the zinc deposit must not be dissolved off with an acid, because acids also act upon nickel. Zinc electrolytically deposited, however, dissolves fairly readily in caustic soda, but it is best to employ a moderately strong warm solution.

**Colour of Deposit.**—Zinc is rather apt to be deposited dark and spongy or speckly. As a rule, good quantitative results can only be obtained when the deposit is quite dense, and of a bluish grey appearance. During the course of the electrolysis, the gas given off often causes the solution to have a milky appearance, but this milkiness usually disappears when the bulk of the zinc has been deposited.

**Cyanide Solution.**—Very good deposits of zinc can be obtained from solutions containing potassium cyanide, but the analytical results are rather uncertain. The zinc salt is dissolved in water, and potassium cyanide solution added in small portions

at a time, until the zinc cyanide, which is at first formed, completely dissolves in the excess of the cyanide. The clear solution so obtained is diluted to the required volume, and electrolysed.

## CONDITIONS.

I.		II.	
C.D.	0.5 to 1.0 ampere.	C.D.	0.5 to 1.1 ampere.
E.M.F.	4.75 to 6.0 volts.	E.M.F.	4.5 to 6.0 volts.
Temp.	normal.	Temp.	50° to 60°.
Time	8 to 16 hours.	Time	6 to 7 hours.

**End Reaction.**—In order to test whether all the zinc has been deposited, a small portion of the solution may be warmed with dilute hydrochloric acid to decompose the cyanide, and treated with a little potassium ferro- or ferricyanide. The electrolysis must be continued until no further precipitate is produced.

**Oxalate Method.**—Deposits of very fine appearance are obtained from solutions containing ammonium oxalate: it is necessary, however, in order to obtain adherent deposits, to keep the electrolyte feebly acid with oxalic acid, or better, tartaric acid. If this precaution is neglected the deposits are usually spongy in character.

The solution is prepared by dissolving about 1 gram. of zinc sulphate in water and adding it to a hot solution of from 4 to 5 gram. of ammonium or potassium oxalate. Zinc oxalate is at first precipitated, but dissolves in the excess of the alkali oxalate. The solution so obtained is electrolysed with a current of 0.5 to 0.6 amperes; the E.M.F. is 3.7 to 4.3 volts. As soon as the electrolysis has commenced, about 3 c.c. of a 5-per-cent. solution of oxalic or tartaric acid is added; further small quantities of the acid are added during the electrolysis, should the solution become neutral or alkaline. The best way to keep the solution acid is to employ the siphon arrangement described on p. 77, Fig. 44. The beaker is filled with a dilute (5 per cent.) solution of oxalic or tartaric acid. The time required is from three to four hours. The drawback to this method is that traces of carbon are often deposited along with the zinc.

The end of the electrolysis may be tested by making alkaline with ammonia, and adding a few drops of ammonium sulphide to a portion of the solution.

**Acetic Acid and Ammonium Acetate.**—To the solution of the zinc salt about 3 gm. of ammonium or sodium acetate is added. The solution is made up to the required volume, and the electrolysis commenced. After a few minutes about 1 c.c. of glacial acetic acid is added, and the electrolysis continued. C.D. 0.5 to 0.8 ampere, E.M.F. 5 to 7 volts. The rate of deposition is accelerated by heating the solution to 35° to 65°. After the electrolysis has proceeded for about an hour, a few drops of ammonia are added, in order to neutralise the excess of acid which has been produced by the decomposition of the zinc sulphate. Time, two to two and a half hours.

**Rochelle Salt and Caustic Alkali.**—Heinrick Paweck<sup>1</sup> has recently suggested a solution containing rochelle salt and caustic soda or potash. To the zinc sulphate solution is added 7 gm. of rochelle salt and 5 gm. of caustic soda. The solution after being made up to the required volume is electrolysed with a C.D. of from 0.1 to 0.5 of an ampere, the E.M.F. being 2.9 to 3.1 volts. The metal is completely deposited in about three or four hours at ordinary temperatures.

**Sulphuric Acid and Sodium Sulphate.**—The solution in this case is made up by dissolving 8 to 10 gm. of sodium sulphate in water, and adding it to the solution of the zinc salt; the electrolysis is then commenced, and, as soon as a thin coating of zinc has been obtained on the electrode, 3 drops (not more) of concentrated sulphuric acid added. When the electrolysis has been in progress from thirty to forty minutes, a few drops of very dilute ammonia are added to neutralise the excess of sulphuric acid. The addition of ammonia is repeated every thirty minutes or so. If this precaution is not taken the zinc may go into solution

<sup>1</sup> *Zeit. f. Elektrochem.*, 1898, 221.

again, owing to the excessive quantity of sulphuric acid which the solution contains. The zinc is deposited as a smooth grey coating of very fine appearance, and is completely deposited in from three to four hours. This method gives one of the finest deposits of zinc, but it requires care.

## CONDITIONS.

I.		II.	
C.D.	. . . 0.4 to 0.6 ampere.	C.D.	. . . 0.6 ampere.
E.M.F.	. . . 3.3 to 4.0 volts.	E.M.F.	. . . 2.5 to 3.0 volts.
Temp.	. . . normal.	Temp.	. . . 50° to 60°.
Time	. . . 3 to 4 hours.	Time	. . . 2 to 3 hours.

## LITERATURE.

Wrightson, *Zeit. f. Anal. Chem.*, XV. 303; Parodi and Masczini, *Ber.*, X. 1098; Riché, *Zeit. f. Anal. Chem.*, XVII. 216; Beilstein and Jawein, *Ber.*, XII. 446; Riché, *Zeit. f. Anal. Chem.*, XXI. 119; Reinhardt and Ihle, *Journ. f. prakt. Chem.*, XXIV. 193; Classen and Von Reiss, *Ber.*, XIV. 1622; Gibbs, *Zeit. f. Anal. Chem.*, XXII. 558; Luckow, *Zeit. f. Anal. Chem.*, XXV. 113; Brand, *Zeit. f. Anal. Chem.*, 28, 581; Warwick, *Zeit. f. Anorg. Chem.*, I. 258; Vortmann, *Ber.*, 24, 2753; Rüdorff, *Zeit. f. Anorg. Chem.*, 1892, 197; Vortmann, *Monatsheft*, XIV. 536; Jordis, *Zeit. f. Elektrochem.*, II. 138, 565, and 655; Classen, *Zeit. f. Elektrochem.*, II. 589; Nissenson, *Ibid.*, 590; Wagner, *Ibid.*, 614; Millot, *Bul. Soc. Chim.*, 37, 339; Nicholson and Avery, *Amer. Chem. Soc.*, 18, 659; Paweck, *Berg. und Hütten Zeit.*, 40, 570; Williams, *British Assoc. Report*, 1898, 295; Smith, *Amer. Chem. Soc.*, 24, 1073; Amberg, *Ber.*, 30, 2489; Hollard, *Bull. Soc. Chim.*, 1903, 20, 266; Hollard and Bertiaux, *Compt. Rendus*, 1903, 136, 1266.

## Silver.

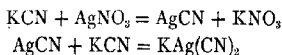
Silver is a metal which can be deposited, either from acid, alkaline, or neutral solutions, and from solutions of its double cyanide. At the same time, there is really only one process which is satisfactory, and that is the cyanide method.

When silver is deposited from solutions containing free nitric acid, the metal generally separates in a crystalline and feathery form, and therefore does not adhere well to the cathode. A further difficulty is that very often a portion of the silver is

deposited at the anode in the form of the peroxide. The addition of small quantities of certain organic acids, such as tartaric or lactic acids, prevents the separation of peroxide, but even when this is done it is only possible to obtain an adherent cathode deposit by the employment of extremely feeble currents. The metal is sometimes deposited at the cathode in a powdery form, and may have a brownish or greyish appearance. This appears to be due to the C.D. being too high.

All silver salts dissolve in ammonia, and attempts have been made to deposit the metal from solutions containing free ammonia. The results, however, are rarely satisfactory; generally speaking the metal is deposited as a brown powder, which does not adhere to the electrode. Neutral solutions also give unsatisfactory results.

**From Potassium Cyanide Solution.**—About 1 grm. of the silver salt is dissolved in water, and a freshly prepared solution of potassium cyanide added. A precipitate is at first formed, but on the further addition of the cyanide solution it dissolves with production of a clear solution, owing to the formation of the so-called double salt of potassium and silver cyanide (see p. 91).



It is very important that the purest obtainable potassium cyanide be employed. That made by passing hydrocyanic acid into alcoholic potassium hydroxide is the best. The deposited metal, when impure cyanide is used, is often brownish in appearance, and is liable to adhere badly. In order to obtain complete solution of the silver salt, it is generally necessary to use from 3 to 4 grm. of potassium cyanide. The conditions necessary are:—

I.		II.	
C.D.	. . . 0.5 to 1.0 ampere.	C.D.	. . . 0.20 to 0.35 ampere.
E.M.F.	. . . 5.6 to 6.0 volts.	E.M.F.	. . . 3.2 to 3.7 volts.
Temp.	. . . 50° to 60°.	Temp.	. . . normal.
Time	. . . 1 to 2 hours.	Time	. . . 4 to 5½ hours.

For running all right a C.D. of from 0.08 to 0.20 amperes may be employed, the E.M.F. being 3.2 to 3.4 volts.

The deposited metal is of a dull silver-white appearance, and adheres firmly to the cathode.

Sometimes the metal appears quite "matt," at other times it possesses a crystalline structure. At times, especially if the current conditions have not been attended to, brown spots make their appearance on the deposited metal; these do not necessarily cause the results to be incorrect, but it is as well to avoid them as far as possible. Gauze or roughed electrodes are the most suitable for silver depositions. Breaking the circuit and washing should be carried out as rapidly as possible, because metallic silver is acted upon by solutions of potassium cyanide.

**End Reaction.**—Treat a small portion of the solution with dilute nitric acid, and boil off the liberated hydrocyanic acid, then add a drop of hydrochloric acid. If no white precipitate or turbidity is produced the electrolysis is completed.

Insoluble silver salts should be warmed with potassium cyanide solution until they are dissolved, and then subjected to electrolysis.

#### LITERATURE.

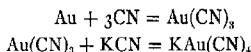
Fresenius and Bergmann, *Zeit. f. Anal. Chem.*, XIX. 324; Krutwig, *Ber.*, XV. 1267; Schucht, *Zeit. f. Anal. Chem.*, 22, 417; *Amer. Chem. Soc.*, IV. 22; Rüdorff, *Zeit. f. Angew. Chem.*, 1892, 5; Smith, *Amer. Chem. Journ.*, XII. 335; Fulweiler and Smith, *Amer. Chem. Soc.*, 23, 583.

#### Gold.

The noble metal gold can be deposited from almost any of its solutions by the passage of the electric current. But satisfactory deposits from acid or alkaline solutions are rarely obtained, the gold usually coming down in the form of a brown non-adherent amorphous precipitate. Indeed, when deposited from acid or alkaline solutions, the colour of the solution may at times become greenish or purplish, owing to the suspension of finely divided particles of gold.

Practically there are three solutions which can be successfully employed for depositing gold. These are the auricyanides, thiosalts, and solutions in ammonium thiocyanate.

On adding a solution of an alkali cyanide to the solution of the gold salt—which, of course, must not be strongly acid—a whitish precipitate is produced. This precipitate, however, readily dissolves when an excess of the cyanide is added, with formation, in the case of potassium cyanide, of **potassium auricyanide**—



Now, as the ions of potassium auricyanide are  $\text{K}^+$  and  $\text{Au}(\text{CN})_4^-$ , the electrolytic separation of gold from such a solution is really a secondary reaction. The explanation given on p. 91 for deposition of copper from cyanide solutions applies also for solutions of gold cyanide.

**Deposition from Cyanide Solutions.**—To the gold solution, from 1 to 2.5 gm. of pure potassium cyanide is added; the colourless solution so obtained is made up to the required volume with distilled water. If the gold solution is strongly acid, it should be partially neutralised with potassium hydrate, or, what is better still, evaporated nearly to dryness, and then taken up with distilled water. The solution of the auricyanide may either be electrolysed at ordinary temperatures or at a temperature of from  $50^\circ$  to  $60^\circ$ .

#### CONDITIONS.

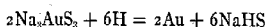
I.		II.	
C.D.	0.15 to 0.4 ampere.	C.D.	0.6 to 0.8 ampere.
E.M.F.	3 to 3.25 volts.	E.M.F.	3 to 3.2 volts.
Temp.	atmospheric.	Temp.	$50^\circ$ to $60^\circ$
Time	10 to 12 hours.	Time	2 to 3 hours.

**Deposition from Solutions of Alkali Sulphides.**—On adding a solution of an alkali sulphide to a solution of a gold salt, a brownish precipitate is at first formed, but this immediately dissolves in excess of the reagent with formation of a gold thiosalt—

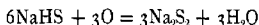


Smith and Wallace have shown that the ammonium thiosalt does not give quantitative results. But satisfactory and quantitative deposits can be obtained by employing potassium or sodium sulphide.

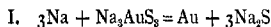
**Course of Reaction.**—The reaction which leads to the deposition of the gold at the cathode is rather involved, but it may perhaps be looked upon as being one of reduction. We have in solution the complex molecule  $\text{Na}_3\text{AuS}_2$ <sup>1</sup> or rather the ions of this complex; the reduction would then take place as follows:—



The sodium hydrogen sulphide being then further oxidised at the anode.



The reaction might, however, be explained on similar lines to those which Hittor employs in the case of the complex cyanides. The sodium aurisulphide is ionised into the cations  $3\text{Na}^+$  and the complex anion  $\text{AuS}_2^-$ . The cation travels to the cathode, and there becomes neutralised, and the liberated sodium then reacts with the water, forming sodium hydrate. The anion migrates to the anode, and is there deposited. The sodium on liberation at the cathode now reacts with some of the unchanged  $\text{Na}_3\text{AuS}_2$ , and liberates gold ions, which in their turn travel to the cathode where they are deposited.



The reformed sodium sulphide dissolves the gold sulphide which has been deposited at the anode, and reforms sodium aurisulphide, and liberates sulphur, which combines with other molecules of sodium sulphide to form polysulphides.

<sup>1</sup> It is not certain that the salt  $\text{Na}_3\text{AuS}_2$  is produced when gold sulphide is dissolved in sodium sulphide; it may be  $\text{Na}_2\text{AuS}_2$ . In fact, this latter salt has been isolated by dissolving  $\text{Au}_2\text{S}_3$  in  $\text{NaHS}$  and pouring the solution into alcohol. But the presence of polysulphides would probably lead to the formation of the first-mentioned salt.





It is, of course, not necessary to assume that the same molecules of sodium sulphide liberated in reaction I. take part in reaction II., because in actual practice there is always a considerable excess of sodium sulphide. Sulphur and oxygen are always liberated to a certain extent at the anode and hydrogen at the cathode, so that at the cathode part of the sodium sulphide will be reduced to sodium hydrogen sulphide, which may, again, at the anode be partially oxidised back to the monosulphide. At the same time the liberated sulphur will produce polysulphides.

The solution for electrolysis is prepared by adding about 30 c.c. saturated or nearly saturated solution of the alkali sulphide to the gold solution; a precipitate is at first formed, but this redissolves, and a clear solution is obtained. The mixture is then diluted to the requisite volume, and electrolysed at the ordinary temperature.

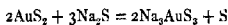
#### CONDITIONS.

C.D. . . . .	0.1 to 0.25 ampere.
E.M.F. . . . .	2 volts.
Time . . . . .	5 to 6 hours,

Both with cyanide and sulphide solutions, brilliant yellow firmly adhering deposits of gold can be obtained.

**Thiocyanate.**—Dissolve 5 to 7 gm. ammonium thiocyanate in 70 to 80 c.c. water, and warm to 50° or 60°; then run in the gold solution with constant stirring. If the solution is cold, a precipitate of gold thiocyanate may be produced, and this is only dissolved on heating the mixture. The solution usually has a red coloration at first, but gradually becomes colourless. Make the solution up to the required bulk with distilled water, and electrolyse.

<sup>1</sup> We might assume that the anion  $\text{AuS}_3'''$  when liberated at the anode gives up an atom of sulphur, and becomes  $\text{AuS}_2$ , this sulphide being known, whereas  $\text{AuS}_3$  has not been isolated. The equation would then be—



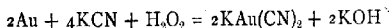
## CONDITIONS.

I.		II.	
C.D.	0.2 to 0.4 ampere.	C.D.	0.2 to 0.4 ampere.
E.M.F.	1.2 to 1.7 volts.	E.M.F.	1.2 to 1.5 volts.
Temp.	normal.	Temp.	40° to 50°.
Time.	4.5 to 5.5 hours.	Time.	1.5 to 2 hours.

The deposit is very often quite as brilliant as that obtained with cyanide or sulphide solutions, but at times it may have a rather smoky appearance; this does not, however, affect the accuracy of the results. Very often during the electrolysis a small quantity of a yellow precipitate separates out. This is canarine (see p. 271), and is due to the oxidising action of anodic oxygen on the thiocyanate; it does not interfere with the deposition of the gold. Potassium thiocyanate, although it gives accurate results, generally gives a deposit of poor appearance.

**End Reaction.**—The small portion of the solution should be boiled with a few drops of concentrated sulphuric acid, to decompose the double salt, and a few drops of stannous chloride added; a purple or violet colour, due to formation of Purple of Cassius, shows that the electrolysis is not yet finished.

**Removal of Deposit.**—The best method to remove the deposit is to cover the electrode with a solution of potassium cyanide, to which has been added 3 or 4 c.c. of hydrogen peroxide, or 2 grm. of sodium peroxide or ammonium persulphate. The deposit is in this way removed in a minute or two. If the solution is warm, the gold goes into solution in a few seconds. When hydrogen peroxide is used the reaction may be expressed thus:—



## LITERATURE.

Luckow, *Zeit. f. Anal. Chem.*, **19**, 14; Brugnatelli, *Phil. Mag.*, **21**, 187; Smith, *Amer. Chem. Journ.*, **XIII**, 206; Smith and Muir, *Amer. Chem. Journ.*, **XIII**, 417; Smith and Wallace, *Ber.*, **25**, 779; Persoz, *Ann. Chem. Pharm.*, **65**, 164; Rüdorff, *Zeit. f. Angew. Chem.*, **1892**, 695; Perkin and Prebble, *Electro-chem. and Met.*, 1904, 111, 490.

## Platinum.

Platinum, like gold, can be deposited from solutions containing free mineral acids; but unlike gold, which from these solutions is deposited in a non-adherent form, it may, if a very feeble current is employed, be deposited in a dense reguline condition. With high currents a deposit of platinum black is invariably produced. Solutions of platinum chloride, containing a few drops of concentrated hydrochloric or sulphuric acid, may be employed.

### CONDITIONS.

C.D. . . . .	0.01 to 0.04 ampere.
E.M.F. . . . .	1.8 volts.
Temp. . . . .	50° to 60°.
Time . . . . .	4.5 to 6 hours.

When a solution containing free phosphoric acid and sodium phosphate is employed, a somewhat heavier current (0.07 to 0.10 amp.) can be used, but in this case a rather longer time is necessary to completely deposit the metal. The platinum electrodes should be coated with copper before being used for the deposition of platinum.

The electrolytic deposition of platinum may be indirectly employed to estimate ammonium and potassium. Both ammonium and potassium are precipitated by means of hydroplatinic acid as the respective platinichlorides. But as they are both distinctly soluble in water, alcohol is always added to complete the precipitation. If the precipitated and washed platinichloride be dissolved in excess of water, and hydrochloric acid added, then the platinum may be electrolytically deposited, and from the amount of platinum obtained the original quantity of potassium or ammonium is readily determined.

### LITERATURE.

Luckow, *Zeit. f. Anorg. Chem.*, **19**, 13; Classen, *Ber.*, **17**, 2467;  
Smith, *Amer. Chem. Journ.*, **13**, 206; Rüdorff, *Zeit. Anorg. Chem.*  
**1892**, 696.

## Palladium

May be deposited from acid solutions in much the same way as platinum, a low current density and a low E.M.F. being necessary. By employing a current of less than 0.1 of an ampere the palladium can be deposited in a bright and reguline condition. Cowper-Coles<sup>1</sup> suggests a solution of palladium-ammonium chloride  $[\text{Pd}(\text{NH}_3 \text{ Cl})_6]$  and ammonium chloride, at a temperature of 25°. This solution does not, however, appear to have been employed by him for analytical purposes. But Smith<sup>2</sup> has obtained good quantitative results by using this solution.

The deposition can be carried out by dissolving the salt in ammonium hydrate; after solution about 30 c.c. more of the ammonium hydrate is added (sp. gr. 0.935) and 100 c.c. of water. The palladium can be deposited overnight by passing a current of 0.07—0.1 ampere. The deposited metal has the appearance of rolled palladium. The platinum electrodes which are employed as cathodes should be first coated with silver or copper.

Amberg<sup>3</sup> finds that by using an anode rotating at about 600 revolutions per minute, he is able to deposit palladium from solutions containing hydrochloric acid. The temperature should be 60° to 65°, and the E.M.F. must not be allowed to exceed 1.25 volts. The rotating anode prevents the formation of peroxide.

## Rhodium.

Smith has shown that rhodium can be rapidly and accurately deposited from solutions containing sodium phosphate and phosphoric acid. The C.D. may conveniently be 0.18. The solution, which at the commencement has a fine purple colour, gradually becomes colourless. As a rule, the deposited metal has a black colour, but is reguline and firm in character.

<sup>1</sup> *Jharbuch*, 1899, VI, 190, and *Eng. and Min. Journ.*, 68, p. 5.

<sup>2</sup> *Electrochemical Analysis*, 3rd edit. 1902, p. 106.

<sup>3</sup> *Zeit. f. Elektrochem.*, 1904, X, 385.

The electrodes upon which the metal is deposited must be coated either with copper or silver.

#### LITERATURE.

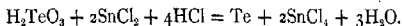
Smith, *Amer. Chem. Soc.*, 5, 201; Joly and Leidié, *Compt. Rendus* 112, 793.

### Tellurium.

Giovanni Pellini<sup>1</sup> deposits tellurium from a solution of tellurium anhydride in hydrochloric acid to which ammonium tartrate has been added. The solution is made up by dissolving 0.1 to 0.2 gm. of the anhydride in 5 c.c. of concentrated hydrochloric acid, to which is then added 100 to 120 c.c. of a cold saturated solution of acid ammonium tartrate. With the following conditions, about 9 hours is required to deposit the tellurium: C.D. 0.01, E.M.F. 1.85 to 2.2 volts, and temperature 55° to 60°.

The tellurium is deposited in a smooth reguline condition, and is at the end of the operation washed with water and alcohol, and dried at 100°. As the tellurium is rather easily oxidised, water which has previously been boiled should be used for washing purposes.

**End Reaction.**—A small portion of the solution is withdrawn, and warmed with stannous chloride and hydrochloric acid: if no brown coloration due to precipitated tellurium is produced, then the electrolysis is completed.



This reaction is very delicate, and is said to show the presence of 0.0001 gm. of tellurium in a solution.

A better method<sup>2</sup> is to dissolve the finely powdered tellurium in a few cubic centimeters of hot concentrated sulphuric acid; a beautiful pink coloration is first produced. When all the tellurium

<sup>1</sup> *Atti. R. Accad. dei. Lincei. Roma* [5], 12, II, 312.

<sup>2</sup> G. Gallo, *Atti. R. Accad. Lincei*, 1904 [v.], 13, i, 713.

has dissolved, the solution is heated until the pink colour vanishes. The white anhydride thus obtained is washed with a little freshly boiled water into a beaker, and then from 80 to 100 c.c. of a 10-per-cent. solution of pyrophosphoric acid or sodium pyrophosphate, freshly boiled, added. The mixture is then electrolysed with a C.D. of 0.1 ampere, the E.M.F. being about 1.6 volts. The solution is hot to commence with, but is allowed to cool as the electrolysis proceeds. Time, 4 to 5 hours.

**Removal of Deposit.**—The deposited tellurium readily dissolves in moderately strong nitric acid.

## Thallium.

Electrolytically, thallium strongly resembles lead, in that it can both be deposited as metal at the cathode or as oxide on the anode. It further resembles lead in the behaviour of the deposited metal, which cannot be washed and dried without undergoing superficial oxidation; it is, therefore, not possible to determine thallium quantitatively as a cathodic deposit. For the determination as oxide, see p. 140. G. Neumann,<sup>1</sup> however, describes a method for analysing thallium which depends upon depositing it as metal from solutions containing ammonium oxalate: the metallic deposit is not weighed, but is treated with hydrochloric acid, and the volume of hydrogen which is evolved is determined. This volume, calculated at N.T.P., is equivalent to the weight of thallium which has been deposited from a weighed quantity of the thallium salt. About 5 to 6 gm. of ammonium oxalate is added to the solution of the thallium salt, and the mixture electrolysed with a current density of about 1 ampere.

**End Reaction.**—The electrolysis is finished when the addition of ammonium sulphide to a small portion of the solution produces no orange precipitate or coloration of thallium sulphide.

The apparatus employed by Neumann is depicted in Fig. 49.

<sup>1</sup> *Ber.*, XXI. 356.

It consists of a small flask, *k*, into which two electrodes are fused; the surface of each electrode is about 9 c.m. The flask is not

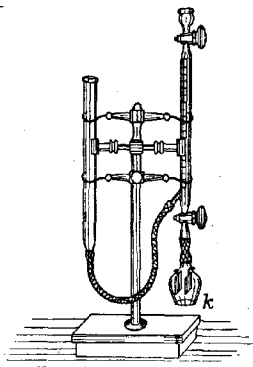


FIG. 49.

fastened on to the gas-measuring apparatus until after the electrolysis has been completed. Before connecting to the measuring apparatus, the solution containing ammonium oxalate and carbonate—the latter produced by the electrolytic decomposition of the ammonium oxalate—is washed out by means of a siphon arrangement, the electrolytic circuit not being broken until the washing is completed. It is then connected up as shown

in Fig. 49, and hydrochloric acid added to dissolve the thallium salt. The method even at best is tiresome, and would only be employed if a large number of determinations were required.

### **Amalgams.**

It has already been noticed that certain metals are very difficult to deposit in a smooth reguline condition, being either deposited in a spongy form, or else they are brittle and show a great tendency to exfoliate. Cadmium, for example, has a marked tendency to be deposited in a spongy and non-adherent form; and it is almost impossible to deposit bismuth in a weighable condition, because the metal either peels off owing to the brittle character of the deposit, or else it is obtained, like cadmium, in a powdery or spongy form. Vortmann and Luckow and others have shown that most metals can be deposited as amalgams if a mercury salt is added to the solution to be electrolysed. The method of procedure is much the same as that adopted for electrolysing mercury solutions; it stands to reason, of course, that

only such solutions as can be employed for depositing mercury may be used. This method can be employed for the deposition of a large variety of metals, but it is only in a few cases that there is any advantage in using it. A few examples will give an idea of how the method may be worked, the student will then be in a position to adopt it in any given case that may appear desirable.

### Cadmium Amalgam.

The cadmium salt is dissolved as usual in about 150 c.c. of distilled water, and then the mercury salt and 1 c.c. of concentrated sulphuric acid added. Mercuric chloride is the most convenient salt of mercury to add, because it is readily obtained pure. For every part of cadmium salt taken (calculated as metallic cadmium), from four to five parts of mercuric chloride (calculated as metallic mercury) should be used. The amalgam then obtained is solid, but when larger quantities of mercury are used, it is fluid or semi-fluid. Thus for 0.5 gm. of cadmium sulphate which contains about 0.2 gm. of metallic cadmium, about 1.5 of mercuric chloride containing 1.1 gm. of metallic mercury would be necessary. When the mercury and cadmium salts have been dissolved, from 2 to 3 c.c. of 20-per-cent. sulphuric acid is added, and the solution made up to 125 to 130 c.c.

#### CONDITIONS.

C.D. . . . .	0.3 to 0.5 ampere.
E.M.F. . . . .	1.9 to 2.3 volts.
Temp. . . . .	60° to 70°.
Time . . . . .	5 to 6 hours.

If during the electrolysis some of the mercury salt is reduced to the mercurous condition, and becomes precipitated, the addition of small quantities of ammonium or potassium persulphate from time to time will cause this to go into solution.

**End Reaction.**—I. This is determined as usual by the addition of a small quantity of sulphuretted hydrogen water to a few cubic centimeters of the solution which is withdrawn for the purpose.



When all the metal has been deposited, the electrode is removed and rapidly washed with distilled water and alcohol, and dried in a desiccator. The drying operation is much more rapid if, after washing with alcohol, the electrode is played upon with the air-blast from the blowpipe for a few minutes. It can then be heated to  $70^{\circ}$  for a few minutes without harm.

II. Ammonium tartrate and free tartaric acid also gives very good results. In this case the cadmium and mercury salt are dissolved up as already described, then 2 gm. of ammonium tartrate and about 3 gm. of tartaric acid added, and the electrolysis conducted under practically the same conditions as those described for the acid solutions.

### **Bismuth Amalgam.**

Owing to the great difficulty in obtaining satisfactory deposits of bismuth, the amalgam method is to be recommended above all others for the electrolytic determination of this metal. The proportions of mercury salt employed to the bismuth salt should be about the same as that recommended for cadmium, namely from four to five times as much mercury as bismuth.

**Solution containing Free Nitric Acid.**—The mercury salt is first dissolved in water, then the bismuth salt added and sufficient nitric acid to cause the bismuth oxy-salt first produced to enter into solution. It is not advantageous to add a large excess of nitric acid, otherwise there is a tendency to obtain an anode deposit of hydrated bismuth oxide. If, however, 1 gm. of tartaric acid is added to the electrolyte, this formation of oxide at the anode is prevented. The tartaric acid should be added before commencing to electrolyse, because when the anode deposit has once formed, it is very difficult to remove.

#### **CONDITIONS.**

C.D. . . . .	0.7 to 1.1 ampere.
E.M.F. . . . .	3.5 to 4 volts.
Temp. . . . .	Normal or $50^{\circ}$ - $60^{\circ}$ .
Time . . . . .	6 to 8 hours.

Sulphuric acid can be employed instead of nitric acid, but, as the results with nitric acid are very satisfactory, there is no advantage to be obtained by its employment.

If the quantity of mercury salt used is too small, the bismuth is often obtained partially as an amalgam and partially as a blackish powder, which covers the surface of the amalgam. The amalgam may be dissolved off with moderately strong nitric acid.

### **Lead Amalgam.**

This metal readily forms an amalgam, and may be deposited as such from solutions containing the lead salt and mercuric chloride, to which is added 5 gm. of ammonium acetate, 3 or 4 c.c. of acetic acid, and a little potassium or sodium nitrite. If the nitrite is not added, a portion at least of the lead will be deposited as peroxide on the anode. The lead amalgam when dry only oxidises very slowly in the air, but when wet the oxidation is somewhat rapid. It should be therefore rapidly washed in water, and then in alcohol, and dried in a desiccator, or at a temperature of 60°, but it should not be left long in the air-bath.

Antimony, tin, zinc, lead, and several other metals can be deposited as amalgams, but since the ordinary methods of electrolysis give good results, the amalgamation method is not often employed. Zinc, as has already been pointed out (p. 118), has a tendency to act upon the platinum electrode, and is only completely removed with considerable trouble; the same difficulty is met with in zinc amalgams.

## CHAPTER IX.

### *METALS DEPOSITED AS OXIDES AT THE ANODE.*

#### **Lead.**

CERTAIN metals, owing to their great tendency to become oxidised, or to their decomposing water, either cannot, under the conditions usually prevailing in electrolytic analysis, be deposited as metals on the cathode, or, if they are deposited, do not give satisfactory analytical results. For example, it is a by no means difficult matter to deposit lead in the metallic state from weakly acid, neutral, or alkaline solutions. But the lead is very apt to be precipitated in a feathery and non-adherent form. There is also a great tendency for the lead to separate at the anode in the form of lead peroxide simultaneously with its deposition at the cathode as metal. Furthermore, although the whole of the lead may, under certain conditions, be deposited in a smooth reguline condition, yet, during the process of washing and drying, a certain amount of superficial oxidation invariably occurs. Thus the results are too high, and are therefore useless for analysis. In depositing lead for analytical purposes, therefore, conditions are employed which prevent the lead from being deposited at the cathode, but cause it to be wholly deposited as peroxide at the anode. The most satisfactory conditions are to employ a solution containing a considerable excess of nitric acid.

**Procedure.**—Dissolve about 1 gram. of lead nitrate in about 30 c.c. of distilled water, then add to the solution about 25 to 35 c.c. concentrated nitric acid, and dilute to the required bulk, which

should not be more than about 175 c.c. The best electrode to employ as anode is the gauze flag electrode, which should be roughened by the sand-blast or a similarly roughened basin. As a rule, the peroxide does not adhere very well upon a polished surface. If during the electrolysis a separation of metallic lead should be noticed at the cathode, a few cubic centimeters more concentrated nitric acid must be added. The electrolysis may either be conducted at ordinary temperature or at from 50° to 55°. It is not advisable to employ much higher temperatures, because there is then a tendency for the peroxide to scale off.

CONDITIONS.

I.		II.	
C.D.	0.5 to 1.8 ampere.	C.D.	1.3 to 1.6 ampere.
E.M.F.	2 to 2.5 volts.	E.M.F.	2.2 to 2.6 volts.
Temp.	Normal.	Temp.	50° to 55°.
Time	2 to 3 hours.	Time	1.5 hours.

At the commencement of the electrolysis a yellowish deposit is obtained, which becomes orange or red, and finally dark brown or black.

**End Reaction.**—Take a few drops of the solution and make alkaline with ammonia, then add a few drops of sulphuretted hydrogen water or ammonium sulphide. A black or brown coloration or precipitate indicates that some lead still remains in the solution. Or make just alkaline with ammonia, then acidify with acetic acid, and add a little potassium chromate or dichromate. If no cloudiness or precipitate of lead chromate is produced, then the electrolysis is finished.

As soon as the deposition is complete, the electrode is removed, rapidly washed with water and alcohol, and heated in an air-bath to 180° or 210° until the weight becomes constant. It is absolutely necessary to heat to this high temperature, because the peroxide is deposited in a more or less hydrated condition.

**Removal of Deposit.**—The deposit of lead peroxide cannot be removed by simply heating with acids. It can, however,

be readily and rapidly dissolved off by warming it with a mixture of nitric acid and glucose. The best mixture is equal volumes of concentrated nitric acid and water, to which is added 4 or 5 grm. of glucose; on gently warming, the deposit quickly dissolves.

The method usually recommended is to place a piece of zinc or copper foil in contact with the electrode, and then immerse in dilute nitric acid, whereby a galvanic couple is formed. This method is quite satisfactory, but the first method described is simpler.

#### LITERATURE.

Kiliani, *Berg. und Hütten Zeit.*, **1883**, 253; Luckow, *Zeit. f. Anal. Chem.*, XIX. 215; Riché, *Zeit. f. Anal. Chem.*, XXI. 117; Hampe, *Zeit. f. Anal. Chem.*, XIII. 183; Classen, *Zeit. f. Anal. Chem.*, XXI. 257; Parodi and Mascazzini, *Ber.*, X. 1098; Riché, *Zeit. f. Anal. Chem.*, XVII. 219; Schucht, *Zeit. f. Anal. Chem.*, XXI. 488; Tenny, *Amer. Chem. Journ.*, 5, 413; Vortmann, *Ber.*, **24**, 2749; Von Giese, *Zeit. f. Elektrochem.*, II. 586 and 598; Rüdorff, *Zeit. f. Angew. Chem.*, **1892**, 198; Warwick, *Zeit. f. Anorg. Chem.*, I. 258; Classen, *Ber.*, **27**, 163; Kreichgauer, *Ber.*, **27**, 315; Classen, *Ber.*, **27**, 2060; Medicus, *Ber.*, **25**, 2490; Neumann, *Chem. Zeitung*, **1898**, 381; Hollard, *Bull. Soc. Chim.*, **19**, 911; Linn, *Amer. Chem. Soc.*, **24**, 435; Marie, *Chem. Zeitung*, **24**, 341 and 480; Nissenson and Neumann, *Chem. Zeitung*, **19**, 1143; Hollard, *Compt. Rendus*, **1903**, **136**, 229.

### Manganese.

It is not possible to deposit manganese from its solutions in the metallic condition, because pure manganese decomposes water. The metal can, however, be deposited at the anode in the form of its peroxide. But it is much more difficult to obtain satisfactory results with manganese than with lead. With lead a large excess of nitric acid can be employed, but with manganese only very small quantities of free acid are permissible. With large amounts permanganic acid is produced, and no deposit of oxide is obtained at the anode.

A very large amount of work has been done upon the electrolytic deposition of manganese, but of the many solutions suggested only a comparatively few give satisfactory results. The main

difficulty in dealing with manganese is to obtain an adherent deposit. The deposit is generally of a more or less friable nature, and crumbles off on washing or drying. It is absolutely essential to employ roughened electrodes. Engels<sup>1</sup> finds that the addition of small quantities of chrome alum causes the deposit to be much more dense and adherent.

**Ammonium Acetate.**—Dissolve the manganese salt,  $\text{MnSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ , which is readily obtained pure, in about 40 or 50 c.c. warm water, then add 8 to 10 gm. of ammonium acetate and 1.5 to 3 gm. of chrome alum. The solution is then made up to the required volume, and electrolysed at a temperature of 75° to 80°.

CONDITIONS.

C.D. . . . .	0.6 to 0.9 ampere.
E.M.F. . . . .	2.8 to 4.2 volts.
Temp. . . . .	75° to 80°.
Time . . . . .	1½ to 2 hours.

Small quantities of acetic acid or mineral acids may be added, but this has no advantage except in cases where separations are being carried out. Chlorides should not be present, because they cause the deposit to be less adherent.

**End Reaction.**—Take a few drops of the solution in a test tube, add about 3 c.c. of concentrated nitric acid, about 1 gm. of red lead. Now boil for a minute or two and dilute with water. If any manganese is present the supernatant liquid will be coloured pink or red owing to the formation of permanganic acid. This reaction is extremely delicate.

When all the manganese has been deposited the electrode is washed with water and alcohol, and then ignited strongly in the blowpipe flame; the ignition must be continued until the whole of the black deposit becomes a dull orange red, owing to the formation of trimanganese tetroxide,  $\text{Mn}_3\text{O}_4$ ; it is then cooled and weighed. The weight of the deposit multiplied by 0.72 gives the weight of metallic manganese.

<sup>1</sup> *Zeit. f. Elektrochem.*, 11., 413.

**Removal of Deposit.**—The trimanganese tetroxide can be readily removed by placing the electrode in warm moderately strong hydrochloric acid.

**Treatment of Permanganates.**—The permanganate is treated with acetic acid, and sufficient hydrogen peroxide to cause the solution to become colourless. The mixture is then boiled with a few cubic centimeters of a solution of a chromate, in order to decompose any excess of hydrogen peroxide. If the hydrogen peroxide is not completely decomposed the deposited manganese oxide does not adhere satisfactorily to the electrode.

In order to cause the adherence of the manganese oxide to the electrode, alcohol may be used instead of chrome alum, but in this case only about 1 grm. of the manganese salt, giving about 0.21 grm. of  $Mn_2O_3$ , should be used, whereas with chrome alum 3 grm. can be safely employed. Acetone has been suggested, but no substance is so satisfactory as chrome alum.

#### LITERATURE.

Luckow, *Zeit. f. Anal. Chem.*, **19**, 17; Schucht, *Zeit. f. Anal. Chem.*, **22**, 493; Classen and Von Reiss, *Ber.*, **14**, 1622; Moore, *Chem. News*, **53**, 209; Smith and Frankel, *Journ. Anal. Chem.*, **3**, 385, and *Chem. News*, **60**, 262; Brand, *Zeit. f. Anal. Chem.*, **28**, 581; Rüdorff, *Zeit. f. Angew. Chem.*, **15**, 6; Classen, *Ber.*, **27**, 2060; Engels, *Zeit. f. Elektrochem.*, **2**, 413, and **3**, 286; Groeger, *Zeit. f. Angew. Chem.*, **1895**, 253; Kaepfel, *Zeit. f. Anorg. Chem.*, **18**, 268; Hollard and Bertiaux, *Compt. Rendus*, **130**, 1266; Koster, *Zeit. f. Elektrochem.*, X, [1904], 533.

#### Thallium.

Heiberg<sup>1</sup> employs the following method for depositing thallium as oxide. About 0.5 grm. of the thallium salt is dissolved in about 100 c.c. of water. Then from 2 to 6 c.c. normal sulphuric acid and 5 to 10 c.c. of acetone added to the solution. After heating to 50° or 55° it is electrolysed, the E.M.F. being kept between 1.7 and 2.3 volts, but towards the end of the operation it may be allowed to rise to 2.5 volts.

<sup>1</sup> *Zeit. f. Anorg. Chem.*, **1903**, **35**, 347.

In order to prevent metallic thallium being deposited at the cathode and to avoid the formation of hydroxide, the solution must be kept acid, but an excess must be avoided because the oxide is somewhat soluble in this acid. The electrode must be roughened, otherwise the deposit may scale off. When the electrolysis is completed, the electrode is washed with water and alcohol, and heated in an air oven to  $160^{\circ}$  or  $165^{\circ}$  for about twenty minutes.

### Uranium.

According to L. G. Kollock and E. Smith<sup>1</sup> and E. F. Korn,<sup>2</sup> uranium can be deposited from solutions containing small quantities of acetic acid and sodium acetate. If the solution is alkaline to commence with, it is not necessary to add the sodium acetate. For every 100 c.c. of solution about 2.5 gm. ammonium or sodium acetate is employed, and then 1 c.c. of 50-per-cent. acetic acid added for every 100 c.c. of solution.

#### CONDITIONS.

C.D. . . . .	.04 to .05 ampere.
E.M.F. . . . .	6 to 8 volts.
Temp. . . . .	$65^{\circ}$ to $70^{\circ}$ .
Time . . . . .	5 to 8 hours.

At the commencement of the electrolysis the uranium is deposited as yellow oxide, then as the black protoxide ( $U_3O_4, 3H_2O$ ). At the end of the operation the electrode is heated to redness, whereby the hydrated oxides are converted to  $U_3O_8$ . The electrode should be cooled in a desiccator. Chromium salts prevent the deposition. When large quantities of uranium are deposited, the oxide is liable to adhere badly to the electrode. This method leaves a good deal to be desired, because there is a great tendency for the uranium to come down on the cathode in the metallic condition and then to be oxidised. When this happens the anode deposit is, of course, unsatisfactory.

<sup>1</sup> *J. Amer. Chem. Soc.*, **23**, 607.

<sup>2</sup> *Ibid.*, **23**, 685.



**End Reaction.**—Add to a few drops of the electrolyte a solution of potassium ferrocyanide; a reddish brown precipitate or a blood-red coloration shows the presence of undeposited uranium.

### **Molybdenum.**

Lily G. Kollock and E. Smith<sup>1</sup> state that when a neutral solution of sodium molybdate is electrolysed, no deposition takes place, but on the addition of a trace of sulphuric acid the solution darkens, and a black anode deposit of sesquioxide is immediately obtained. The molybdenum salt is dissolved in water, made up to 125 c.c., and 0.1 to 0.2 c.c. of concentrated sulphuric acid added, and the solution electrolysed. It is advisable to add 3 or 4 gm. of ammonium sulphate to the solution, in order to increase the conductivity.

#### CONDITIONS.

C.D. . . . .	0.02 to 0.05 ampere.
E.M.F. . . . .	2.0 to 2.25 volts.
Temp. . . . .	70° to 85°.
Time . . . . .	2.75 to 4.75 hours.

As soon as the electrolysis is finished the deposit is washed with water, treated with nitric acid, and evaporated to dryness; by this means a white powder of molybdenum trioxide  $\text{MoO}_3$  is produced. If, as is sometimes the case, there are blue specks noticeable in the white trioxide, it must again be evaporated to dryness with nitric acid.

**End Reaction.**—Acidify a small portion of the solution with hydrochloric acid, add a few cubic centimeters of a solution of ammonium thiocyanate and then a small piece of zinc. If a blood-red coloration is produced, then the electrolysis is not complete. Phosphoric acid does not destroy this coloration, but it destroys the red coloration of ferric thiocyanate.

<sup>1</sup> *Journ. Amer. Chem. Soc.*, **23**, 669.

## Vanadium.

P. Truchot<sup>1</sup> has succeeded in estimating vanadium as its oxide  $V_2O_5$ . A small quantity of ammonia is added to the solution of the vanadate, and the mixture subjected to electrolysis.

### CONDITIONS.

C.D. . . . .	0.4 ampere.
E.M.F. . . . .	2 to 2.5 volts.
Temp. . . . .	85° to 90°.
Time . . . . .	8 to 10 hours.

The solution should not contain more than 0.25 gm. of  $V_2O_5$  to the litre. During the electrolysis the water lost by evaporation should be made up, by employing the siphon arrangement recommended on p. 77. The hydrated oxide is deposited on the anode as an adherent brown coating. At the end of the reaction it is washed with water and alcohol, and heated until it melts; when sufficiently heated it is completely converted into the pentoxide, which is of an orange-red colour. If after ignition the deposit has a greenish or bluish colour, it must be remelted until it becomes homogeneously orange-red.

Considering the extremely dilute solutions which require to be employed, this method can hardly be considered of any great importance.

## The Halogens.

Vortmann has shown that if a solution of a halogen salt is electrolysed, using a silver anode, the halogen unites with the silver. The increase in weight, therefore, of the anode shows the amount of halogen which has been deposited. It is further possible, by carefully regulating the voltage, to separate a mixture of the halogens, iodine being first deposited out at a lower voltage, and then, by increasing the E.M.F. and changing the electrode, the bromine is precipitated out, and may in turn be weighed.

<sup>1</sup> *Jahrbuch*, 1902, IX. 374.

The chloride which remains in solution can be determined by titration with normal or decinormal silver nitrate.

**Method.**—The silver anode should be made of wire coiled into a flat spiral, as shown in the case of platinum, Fig. 42, p. 76. The cathode may be either of copper, nickel, or platinum. The solution to be electrolysed is made alkaline, and an alkali tartrate added. It is not necessary to notice the C.D., but in hot solutions the E.M.F. should not rise above 1.3 volts. In cold solutions it must not exceed 2 volts. The end of the process can be determined by acidifying a portion of the solution, adding a little starch paste and a few drops of chlorine water. If there is any iodine left in the solution, its presence is shown by the formation of a blue colour of iodide of starch.

When the operation is completed, the anode is well washed in distilled water and dried in an air-bath; the temperature should be nearly sufficient to melt the silver iodide.

Should there be bromine in the solution, the E.M.F. is increased and the bromine deposited upon a clean silver anode.

E. Müller recommends for the quantitative estimation of iodine in presence of bromine and chlorine the addition of small quantities of a soluble chromate to the electrolyte, because he finds that with an E.M.F. too low to discharge the  $\text{Br}'$  and  $\text{Cl}'$  ions the whole of the iodide is oxidised to iodate. A freshly platinised platinum electrode is employed; the E.M.F. will be about 1.6 volts and the C.D. 0.10 to 0.01 ampere. The time required to completely oxidise about 0.10 of a grm. of iodide to iodate is about twenty hours.

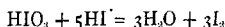
In order to carry out the electrolysis Müller recommends the preparation of the following reagents:—

I. Potassium dichromate, 1 c.c. =  $10.6 \text{ c.c.} \frac{N}{100}$  thiosulphate solution.

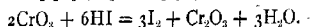
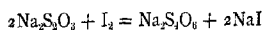
II. Normal potassium hydrate.

III. Potassium iodide, 1 c.c. =  $9.13 \text{ c.c.} \frac{N}{100}$  silver nitrate solution.

As an exercise to determine the iodine alone, other halogens not being present, take 2 c.c. of solution I., 1 c.c. of solution II., and 10 c.c. of solution III., then dilute with 90 c.c. water. At the end of the electrolysis, excess of potassium iodide is added, and the solution acidulated with sulphuric acid, iodine being thereby liberated—



the liberated iodine is then titrated with  $\frac{\text{N}}{10}$  sodium thiosulphate as usual, the number of cubic centimeters used up by the chromate being subtracted from the total number of cubic centimeters employed.



**In presence of chlorine:** take 2 c.c. solution I., 1 c.c. solution II., and 1 c.c. solution III., then add 100 c.c. of a saturated solution of sodium chloride. Time required for electrolysis, twenty hours.

**In presence of bromine:** 2 c.c. solution I., 1 c.c. solution II., and 1 c.c. solution III., then 100 c.c. of a solution of normal potassium bromide. Time, twenty-two hours.

It is most important to keep the anode completely covered; the E.M.F. must not be allowed to rise above 1.61 or 1.62, otherwise the chloride and bromide will take part in the electrolysis. Metals of the alkaline earths must be removed before commencing the electrolysis.

#### LITERATURE.

Whitfield, *Amer. Chem. Journ.*, **8**, 421; Vortmann, *Elektro-technische Zeit.*, **1**, 137, and **11**, 169; Müller, *Ber.*, **35**, 950.

### Determination of Nitric Acid and Nitrates.

If a solution of a nitrate or nitric acid is acidified with sulphuric acid and then electrolysed, the nitrate is not reduced

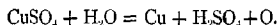
to ammonia. But Luckow has shown that when an acidified solution, which also contains a metallic salt such as copper sulphate, is electrolysed, the metal is deposited at the cathode, and at the same time the nitric acid is reduced to ammonia.

**Method.**—About equal quantities of copper sulphate and of the nitrate to be analysed are taken; the solution is then acidified with sulphuric acid and electrolysed. The end of the reduction may be shown by adding a drop of the solution to a trace of brucine on a watch-glass, and then adding a drop of concentrated sulphuric acid; if no pink coloration is produced then the reduction is completed. W. H. Easton<sup>1</sup> recommends a C.D. of 1 ampere and the addition of about 30 c.c. of dilute sulphuric acid (sp. gr. 1.062).

As soon as the reduction is finished the solution is transferred to a flask, made alkaline with caustic alkali, and the ammonia distilled over into a known volume of  $\frac{N}{2}$  sulphuric acid. On titrating the excess of acid with  $\frac{N}{2}$  caustic soda, the amount of ammonia produced by the reduction of the nitrate is readily determined.

### Preparation of Standard Sulphuric Acid.

When a solution of pure copper sulphate is electrolysed, the copper is deposited out, and an equivalent quantity of sulphuric acid remains in the solution—



In order to know the exact quantity of the sulphuric acid in the solution, it is therefore only necessary to weigh the amount of copper which has been deposited, because 49 parts of sulphuric acid will invariably be produced from 31.8 parts of copper, which was originally present as copper sulphate. This method is hardly

<sup>1</sup> *J. Amer. Chem. Soc.*, 25, 1039.

one which could be employed for preparing standard sulphuric acid in quantity, but it could very usefully be adopted for standardising alkaline solutions.

When it is desired to prepare a given quantity of an exact normal or decinormal solution, it is then necessary to exactly weigh out the pure crystallised copper sulphate before electrolysis. The amount of copper deposited then serves as a check on the original weighing. Thus, for example, 1.249 grm. of pure crystallised copper sulphate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) would yield on electrolysis 0.49 grm. of sulphuric acid, which on dilution to 100 c.c. would be exactly decinormal.

Dr. C. Kohn<sup>1</sup> recommends the employment of a C.D. of 0.2 to 0.4 ampere. If a high current density is used, there is a tendency for the copper to become spongy; it is then difficult to weigh, and it might fall off and contaminate the solution.

## Arsenic.

It is not possible to deposit arsenic quantitatively in the metallic condition, neither can it be precipitated at the anode as oxide. Arsenic is a substance which is very readily converted by nascent hydrogen to arseniuretted hydrogen, its gaseous hydride  $\text{AsH}_3$ ; for this reason the electrolytic methods of analysis are not employed for analysing arsenic compounds. It is, however, possible to estimate very small quantities of arsenic contained in food, etc., by electrolysis. The process consists of evolving electrolytic hydrogen in presence of the arsenic whereby the arsenic is converted into arseniuretted hydrogen. The gaseous hydride is then passed through a glass tube, heated with a small bunsen burner. This decomposes the hydride, and the arsenic is deposited upon the tube in the form of a mirror. In order now to estimate the amount of the arsenic the mirror is compared with the mirror on a number of tubes which have been prepared from known quantities of arsenic.

In 1812 Fischer<sup>2</sup> suggested the employment of the electric

<sup>1</sup> *Soc. Chem. Ind.*, 1900, 962.

<sup>2</sup> *Gilbert's Ann.*, 42, 92.

current to detect the presence of very small quantities of arsenic. It was again suggested by Bloxam<sup>1</sup> in 1861, but the apparatus as then suggested had several disadvantages, and never came into practical use. Since then various modifications have been suggested by different authors, and, in 1903, Dr. T. E. Thorpe<sup>2</sup> published a new form of the apparatus, which has been successfully employed for the analysis of traces of arsenic in food, beer,

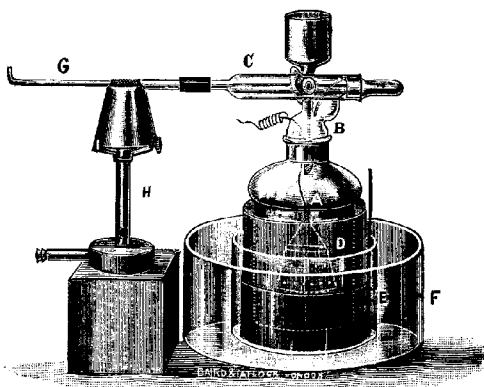


FIG. 50.

and other substances. The apparatus consists of a platinum cathode, A, hung in a glass cylindrical vessel, B, which is open at the end and fits into a Pukal porous cell, D. The porous cell is surrounded by the anode, and stands in an outer vessel, E. The upper portion of the cylinder B is open, and has a ground neck for the insertion of the drying-tube c, which is filled with anhydrous calcium chloride and also carries the funnel, which is fitted with a tap, through which the solution to be tested can be run in. A capillary tube, G, is connected on to the end of the calcium chloride tube c. The middle of the capillary tube is

<sup>1</sup> *Quart. Journ. Chem. Soc.*, 1861, 18, pp. 12 and 338.

<sup>2</sup> *Journ. Chem. Soc.*, 1903.

heated by means of the small bunsen burner H, and is surrounded where the flame heats it with a piece of platinum or iron wire gauze, to prevent the tube being fused. The whole apparatus is placed in a vessel, F, containing cold water, to prevent undue heating during electrolysis.

**Method of Working.**—The apparatus is carefully washed with distilled water. The outer cell E is filled with dilute sulphuric acid, 30 per cent. Then the dilute sulphuric acid is run into the porous cell by means of the funnel. (The porous cell should be soaked in dilute sulphuric acid for about half an hour before being used.) As soon as all the connections are made, the bunsen burner is placed in position, but not lighted, and the current is passed. A current of about 5 amperes should be used, because then the escaping hydrogen issues at sufficient speed to produce a flame of about 3 mm. in size. As soon as all the air has been driven out, which usually occupies about ten minutes, the issuing hydrogen is ignited and the bunsen burner lighted. If after about fifteen minutes no brown ring makes its appearance, then the reagents may be considered free from arsenic. About 2 c.c. of amyl alcohol (to prevent frothing) may be run in,<sup>1</sup> and then the solution to be tested. At the end of thirty minutes the capillary tube is sealed off and the open end also fused together. The mirror is then compared with the standard mirrors obtained from various quantities of arsenic.

**Preparation of Standard Deposit.**—Pure resublimed arsenious oxide is ground up in an agate mortar and dried at 100°. Then 0.1 gm. is carefully weighed and washed into a 1-litre flask, the flask then being filled to the mark with distilled water. Every 1 c.c. of this solution therefore contains 0.0001 gm. of arsenious oxide. Now take 100 c.c. of this solution, and dilute to 1 litre. This second solution contains 0.00001 gm. of arsenious acid to each 1 c.c. or 0.01 mg. Standard tubes containing 0.004, 0.006, 0.008, 0.010, etc., mg. can then be prepared.

<sup>1</sup> The addition of amyl alcohol rather diminishes the delicacy of the method; therefore, unless there is considerable frothing, it is not to be recommended.



When food stuffs are being examined for arsenic, Dr. Thorpe considers it best, in order to prepare a standard mirror, to take a portion of the food stuff—arsenic free—and add the known quantity of arsenic to this before proceeding to electrolyse it. Then when the suspected food is examined, the conditions are the same as when the standard tube was prepared. For general work, however, this precaution is not necessary.

S. R. Trotman<sup>1</sup> recommends the adoption of a parchment membrane in place of the porous Pukal cell, as he considers this decreases the resistance and thus makes the apparatus more sensitive.

Dr. Sand and J. E. Hackford<sup>2</sup> use the parchment membrane, but they also employ a heavy leaf cathode and a lead anode. This causes their apparatus to be much cheaper than that of Dr. Thorpe, and they claim equal accuracy—in fact, it is stated the apparatus is more delicate, because the hydrogen is given off from the surface of the lead electrode at a higher voltage than from one of platinum. When platinum is employed as cathode, the hydrogen evolved has not sufficient energy to reduce arsenates to arsenites and then to  $\text{AsH}_3$ , therefore it is necessary when dealing with arsenates to first reduce with sulphurous acid before electrolysing. But with lead electrodes, owing to the higher tension at which the hydrogen is liberated, this preliminary treatment is not necessary. Full particulars of the apparatus of Sand and Hackford can be found in the original paper.

<sup>1</sup> *J. Soc. Chem. Ind.*, **23**, 177.

<sup>2</sup> *Chem. Soc.*, **85**, 1018.

## CHAPTER X.

### *SEPARATION OF THE METALS.*

THE electrolytic separation of the metals may be brought about in several ways. When various metals occur together, we do not generally make a complete separation by electro-chemical methods only, without bringing to our aid separations which are purely chemical in character. But by a judicious employment of electro-chemical and chemical means, separations of the most complex mixtures can be brought about, which by the employment of only electro-chemical or only of chemical methods might be matters of considerable difficulty. The purely electro-chemical methods of separation may be classed under five heads :—

**I. Separation by means of Variable Potential.**—As the decomposition values of the various salts of metals vary, it is possible to separate the metals by keeping a constant E.M.F., which is high enough to decompose the metal whose salt has the lower decomposition value, but too low to deposit the metal of higher decomposition value. This method is only applicable when the decomposition values do not lie too close together.

**II. Separation by depositing one Metal on the Cathode and the other on the Anode as Oxide.**—It has already been found that certain metals can be deposited on the anode as oxides, while other metals in the same solution are deposited in the metallic condition on the cathode. For example, in a solution acidified with nitric acid, copper is deposited at the cathode in the metallic form, but lead is precipitated on the anode as lead peroxide.

**III. Separation by choice of Electrolyte.**—Some metals

are deposited from acid solutions, other metals can only be precipitated from solutions which are neutral or alkaline; certain metals are deposited from strongly acid solutions, but others can only be deposited from dilute acid solutions.

#### IV. Artificial alteration of Decomposition Value.—

This can be effected by the formation of complex salts, such as the so-called double cyanides and the thiosulphides, or by altering the state of oxidation of the salt.

**V. Hollard's Methods.**—The first method of Hollard, which we will call A, really comes under the heading IV. It depends upon the reduction of the resistance of the bath by suppressing the gas formation at the anode. This is carried out by the addition of reducing-agents, such as sulphurous acid, to the bath.

Although, as shown under I., metals can be separated from each other by varying the potential, only metals whose polarisation potentials are lower than that of hydrogen can be satisfactorily separated in this manner. Owing to the necessity of maintaining a low potential, the current to deposit the metal is always weak, but when the polarisation potential is higher than that of hydrogen, then there is a greater tendency for hydrogen to separate than for the metal, so that the deposition of the metal is never complete. The metal may be fairly readily deposited at first, but when towards the end of the electrolysis the concentration of the metallic ions becomes low, then the liberation of hydrogen completely prevents any further deposition, the hydrogen ions alone conveying the current.

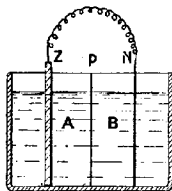


FIG. 51.

B. Secondly, Hollard finds, that when a soluble anode is employed, the oxygen liberation is suppressed. The method is shown diagrammatically in Fig. 51: A is a zinc anode which is connected to the platinum cathode B by the wire ZN. The anode and cathode are separated by means of a parchment membrane or porous diaphragm, &c.

Suppose, now, that it is desired in a certain solution to separate

nickel from zinc. This solution is placed in the cell containing the cathode, a solution of an indifferent substance, such as magnesium sulphate, being placed in the anode compartment. By this means a reversible cell of two liquids of the Daniell type is made. The current passes through the external circuit from the platinum to the zinc, and through the liquid from the zinc to the platinum. Nickel thus becomes deposited out, and the zinc remains in solution.

**C. Influence of the Nature of the Cathode.**—By taking a cathode made of the same metal as that to be deposited the polarisation potential of hydrogen is raised above the polarisation potential of the metal to be deposited. By this means it is possible to precipitate such metals as lead, tin, and cadmium from solutions which are strongly acid. Cadmium and zinc can, for example, be separated by employing a platinum electrode on which a coating of cadmium has been already deposited. The cadmium is then deposited, but the zinc remains in solution.

It is not intended to set forth all the possible separations of the different metals; only those of the most importance will be given. But the student who has carefully worked through the depositions of the metals from pure salt solutions should be in a position, after a little experience, to work out methods of separation for himself. When the separation is one in which several metals are to be dealt with, it is almost invariably necessary to combine electro-chemical and chemical methods. The separations will be found under the heading of the individual metals. The best form of electrode to use for the separation of the metals is generally the flag electrode (p. 79), because, when the flag electrode is removed from a solution, only a very small quantity of the solution which contains the other metal or metals adheres to the electrode, and this can generally be quite easily washed off into the beaker with the wash bottle.

Generally the current density and E.M.F. will not be stated, except when it is different from that required in depositing from pure solutions; in all other cases the reference to the method will be given.

## COPPER.

Copper is one of the most readily deposited of metals, because it can be thrown out from strongly acid solutions, alkaline solutions, or solutions containing potassium cyanide.

### Copper from Iron.

For practice in carrying out the separation of copper and iron, prepare a solution containing about 1 gram. each of copper sulphate and ferrous ammonium sulphate or of iron alum. Acidify this solution with 2.5 to 3 c.c. of concentrated sulphuric acid, and dilute to 130 or 150 c.c. Electrolyse with a current density of about 1 ampere at ordinary temperatures. The time required to deposit all the copper will be between three and four hours; with warm solutions the copper can be completely deposited under three hours. The end reaction is found in the usual way by lowering the cathode slightly into the solution; if after ten minutes no deposit has taken place on the freshly immersed cathode surface, the deposition is complete. When all the copper is deposited the electrode is removed, and washed and dried as usual. (See p. 87.)

The solution, which now only contains the iron, has about 4 gram. of ammonium oxalate or tartrate added to it, and is then neutralised with ammonia. If too much ammonia is accidentally added, the solution may be neutralised back with oxalic or tartaric acid. The mixture is now electrolysed at a temperature of 40° to 50°, with a C.D. of 0.8 to 1 ampere. (See p. 101.)

The only drawback to employing sulphuric acid in the separation is, that the copper is very often deposited in a spongy and non-adherent form. If, instead of using sulphuric acid, 4 to 5 c.c. of nitric acid is taken, then the copper is deposited in a dense and firm condition (p. 86). But when nitric acid is used, and therefore, on neutralising, nitrates are present, the iron is often partially precipitated as ferric hydrate. For this reason, in this case, it is best to add excess of ammonia, and precipitate the iron as ferric

hydrate. The precipitate is filtered off, washed with hot water, and then dissolved in a little warm solution of tartaric or oxalic acid. The solution is then neutralised with ammonia and electrolysed as usual. Or the solution may be evaporated nearly to dryness, with a little sulphuric acid, in order to expel the nitric acid. The salts are then dissolved in water, 3 or 4 gm. of tartaric or oxalic acid added, and the solution neutralised with ammonia.

### **Copper from Cobalt or Nickel.**

The copper is deposited as in the separation from iron, from solutions acidified with sulphuric or with nitric acid. The same remarks with reference to the character of the deposited copper apply in this case. Sulphuric acid has a tendency to cause a poorly adhering deposit, but a good deposit is invariably obtained when nitric acid is used.

If sulphuric acid is taken as the electrolyte, and the other metal is nickel, it is only necessary to make the solution strongly alkaline with ammonia, after the copper has been deposited, and then to deposit the nickel directly from this solution (p. 92).

If the other metal is cobalt, then, after depositing out the copper, the solution is made slightly alkaline with ammonia, and then just acid with phosphoric acid; after which 3 gm. ammonium dihydrogen phosphate is added, and the cobalt deposited as usual from an acid phosphate solution (p. 98).

Both cobalt and nickel are deposited with difficulty from solutions containing nitrates; therefore, if nitric acid has been employed for depositing the copper, the solution should be evaporated down nearly to dryness with a little sulphuric acid to drive off the nitric acid. It is then diluted with water, and treated as above described. Only in this case the borate method may be used for depositing the nickel (p. 95).

### Copper from Cadmium.

In separating copper from cadmium, either nitric acid or sulphuric acid can be employed, but the former gives the better results.

Smith and Wallace<sup>1</sup> recommend the addition of 2 c.c. nitric acid to every 100 c.c. of solution, the solution to be electrolysed at a temperature of 50°, and with an E.M.F. of 2.5 volts, the current under these conditions will be 0.1 ampere.

Heidenreich<sup>2</sup> states that good results are obtained when 15 c.c. sulphuric acid (1.09 sp. gr.) is added to the solution, and the electrolysis conducted at an E.M.F. not exceeding 1.85 volts.

When the whole of the copper has been deposited, the solution is made just alkaline with sodium hydrate, and sufficient potassium cyanide added to dissolve the precipitate of cadmium cyanide first formed. The solution is then electrolysed as described on p. 115.

Smith also recommends separation by employment of a solution containing hydrogen disodium phosphate and free phosphoric acid. He takes 20 c.c. of a solution of hydrogen disodium phosphate (sp. gr. 1.035) and 10 c.c. of a solution of phosphoric acid (sp. gr. 1.347); temperature, 60°, with a current of 0.07 to 0.08 ampere, and a potential of 2.5 volts. The time required to deposit the copper is about three hours.

The cadmium can be deposited first, the copper remaining in solution if excess of potassium cyanide is added to the solution of the mixed salts. It has already been noticed under copper, p. 90, that when excess of potassium cyanide is present the deposition of the copper is prevented; this, however, is not the case with cadmium.

In order to carry out this operation, sufficient potassium cyanide is added to the mixed solution to dissolve the first-formed precipitate of copper and cadmium cyanides, and then 3 to 4 grm. more potassium cyanide added. The E.M.F. should

<sup>1</sup> *Amer. Chem. Soc.*, **19**, 870; *Amer. Chem. Journ.*, **12**, 329.

<sup>2</sup> *Ber.*, **28**, 1585.

not be allowed to exceed 2.6 or 2.7 volts, otherwise a portion of the copper may be precipitated as an alloy with the cadmium. The cyanide method for depositing cadmium is certainly the most sure, but it generally requires from six to eight hours.

### **Copper from Zinc.**

Acid solutions can be employed in this separation, provided that the acid is not too dilute. Nitric acid, although it yields the best results for copper, has the disadvantage—already frequently noted with other metals—of preventing a satisfactory subsequent deposition of the zinc. When, therefore, nitric acid is employed, the solution must, after the copper has been deposited, be evaporated down almost to dryness with a little sulphuric acid, in order to drive off the nitric acid. The zinc salt remaining is then dissolved in water, and the excess of sulphuric acid neutralised with ammonia. Solutions containing a trace of sulphuric acid give very good deposits of zinc (p. 120); the precaution of adding a little ammonia to neutralise the acid freed as the zinc is deposited must not be omitted, otherwise the deposit may commence to dissolve again.

The deposition of zinc from cyanide solutions is not satisfactory, but Classen's oxalate method gives very good results. This method, with the necessary precautions, is set out on p. 119.

### **Copper from Silver.**

In the separation of copper from silver the method usually employed depends upon variation of potential. Several solutions may be used; for example, solutions acidified with nitric acid or the double cyanide can be employed. As a low E.M.F. is of necessity employed in the operation, it follows that the current is also low, and therefore the separation requires some little time. When a solution containing nitric acid is employed the potential should not exceed 1.3 to 1.4 volts, otherwise copper will be deposited along with the silver. The chief objection to using



a solution acidified with nitric acid is the form in which the silver comes down, it being very often of a crystalline nature, and the crystals are apt to become detached when the deposit is being washed.

The regulation of the E.M.F. is of very great importance; the source from which the current is obtained should not have a potential much above that which is required in the experiment. One difficulty is, that when most of the silver has been deposited and the electrolyte becomes attenuated in silver ions, the E.M.F. rises, and unless the experiment is being carefully watched, it will be found that towards the end of the operation an alloy of copper and silver instead of pure silver has been obtained.

**Method for regulating the Potential.**—When a long bath of copper sulphate has two electrodes placed at either end, the central space being free, a considerable E.M.F. is necessary in order to cause a current of any intensity to pass through the bath. Now, when in between the two electrodes plates of copper are hung in such a manner that they make no electrical contact, it is found that these plates become di-polar—the one

side becoming anode and the other side cathode.

The drop in potential between the plates is according to their distance apart.

The drop in potential in a 10-per-cent. copper sulphate solution is about 0.3 of a volt, when the plates are fixed about a centimeter apart, and a current of 1 ampere is passing through the cell. Such a

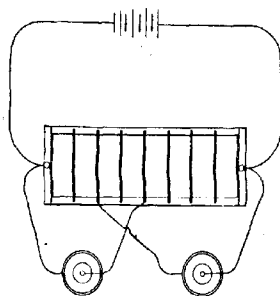


FIG. 52.

cell is shown diagrammatically in Fig. 52.

In the figure there are seven plates hung independently; two electrolyzing cells are shown, which are connected respectively

between the  $-$  pole and plate No. 4, and between plate No. 2 and the  $+$  pole. If, now, the drop in potential is 0.3 volt between each plate, it follows that by taking five plates a shunted current will be obtained, having an E.M.F. of 1.5 volts. Therefore the highest potential the bath could possibly show would be 1.5 volts. When higher potentials are required, the distance between the two end electrodes is increased, with a consequent rise in E.M.F.

It is not, of course, necessary to have so many plates in between, but by having a number of plates the current can be shunted off for a number of experiments. The main portion of the current passes, of course, directly through the copper bath, and any slight variation in the shunt circuit will have no practical effect upon the voltage. By increasing the current in the copper bath, and therefore the E.M.F., the potential of the shunt circuit will also be raised. It is advisable to reverse the current at the terminals of the copper bath every twenty-four hours or so, in order to keep the copper plates in condition.

Such an arrangement as this can, of course, only be employed where low currents are required.

Another good method for obtaining low voltages, but which does not admit of such delicate graduation as the one just described, is to use cupron elements (p. 48), the E.M.F. of each cell being about 0.8 volt. Therefore 2 cells coupled in series give a potential of 1.6, and 3 cells 2.4 volts. A thermopile can also be used with advantage.

**Copper from Silver in Cyanide Solution.**—Both copper and silver can be readily deposited from solutions containing potassium cyanide in which they both form complex anions. But the silver is deposited at a lower potential than is required to precipitate the copper. In order that silver only may be deposited, the potential must not be allowed to rise above about 1.6 to 1.7 volts. It is also advisable to have a considerable quantity of potassium cyanide present, because the E.M.F. necessary to deposit copper is higher when the concentration of the cyanide is fairly high. The solution is made up by dissolving

the copper and silver salts in water, and adding sufficient of a solution of potassium cyanide to dissolve the precipitate first formed, then about another 3 or 4 gm. of potassium cyanide is added to the solution. After all the silver has been deposited, which can be ascertained by boiling a few cubic centimeters of the solution with a drop or two of hydrochloric acid—this portion withdrawn must be returned again,—the copper can be deposited by raising the E.M.F. Since, however, the cyanide solution is rather strong for the satisfactory deposition of copper, a little sulphuric acid is added to it in order to decompose the excess of potassium cyanide—*this must, of course, be done in the draught cupboard.*

**Separation in Nitric Acid Solutions.**<sup>1</sup>—In solutions containing nitric acid the silver is deposited without the copper if the potential is not allowed to rise above 1.3 to 1.4 volts. As soon as all the silver is deposited, the E.M.F. is increased, and this causes the copper to be deposited.

The separation of silver by either of these methods may take a considerable time if there is any quantity of the silver salt present, from ten to fifteen hours often being required to remove less than 0.5 gm. of silver. Therefore these separations are best conducted overnight.

### Copper from Mercury.

These metals may be separated by means of solution in potassium cyanide, the mercury being deposited out at a lower potential than the copper. Smith and Spencer<sup>2</sup> recommend to electrolyse at a temperature of 55° to 70°, with a C.D. of 0.06 to 0.08 ampere; the E.M.F. must not exceed 2.5 volts. About 0.1 gm. mercury can thus be deposited in from three to four hours. For this quantity of mercury, and an equal quantity of copper,

<sup>1</sup> Kiliani, *Berg. und Hütten Zeit.*, 1883, 375; Freudenburg, *Zeit. f. Phys. Chem.*, 12, 197.

<sup>2</sup> *Amer. Chem. Soc.*, 1894.

about 1 to 2 grm. of potassium cyanide is sufficient. When all the mercury is deposited out, the current is increased, and the copper is in turn precipitated.

### **Copper from Lead.**

By using solutions containing a considerable quantity of nitric acid, there is no difficulty in depositing copper and lead simultaneously. A sand-blasted flag electrode or roughened basin is made the anode, the cathode being of the usual wire form generally employed as the anode.

To every 100 c.c. of solution about 7 to 8 grm. of concentrated nitric acid is added, and the solution electrolysed at a temperature of 55° to 60°. The C.D. may be from 1 to 1.75 amperes, and the E.M.F. will be about 1.4 to 1.5 volts.

The lead is all deposited in about an hour and a half, but the copper takes considerably longer to deposit. If the amount of copper is large, it is better to stop the electrolysis when the whole of the lead has been thrown out, and remove the electrode on which the peroxide has been deposited. A fresh cathode of larger surface is then placed in the solution, and the electrolysis of the copper recommenced, the original cathode being now the anode. This change of electrode is rather tiresome when a basin anode has been employed, but it entails no trouble with a flag electrode. The deposition of the copper is carried out according to the usual method of operation in solutions containing nitric acid (p. 86). It is sometimes advisable to partially neutralise the excess of nitric acid after the lead has been deposited, because copper is only slowly thrown out from solutions containing very large quantities of nitric acid.

### **Copper from Manganese.**

Copper and manganese can be separated in much the same manner as copper and lead, only if nitric acid is employed its amount must not exceed 3 or 4 per cent., because with stronger

solutions of nitric acid permanganic acid is produced and no anode deposit is formed. It will be remembered that considerable difficulty is experienced in obtaining a satisfactory and adherent anode deposit of manganese oxide; in fact, the only really satisfactory method is the one described on p. 139. There it is mentioned that in cases of separation small quantities of a mineral acid may be added.

The solution is therefore made up by dissolving the manganese and copper salt in water, adding about 2 to 3 gm. of chrome alum, about 8 gm. of ammonium acetate, and 2 c.c. of sulphuric acid. This mixture is then electrolysed with a C.D. of 0.6 to 1 ampere, at a temperature of  $75^{\circ}$  to  $80^{\circ}$ . The copper will probably be deposited in a badly adhering form, and it may be advisable to redissolve it in nitric acid and re-deposit it.

With care the copper and manganese can be separated from solutions containing about 2 to 3 per cent. of nitric acid; but the manganese deposit is rarely satisfactory, although the copper is generally quite good. But as the manganese deposit is not very readily dissolved up again, this method is not of much value, owing to the difficulty of obtaining a solution of the manganese if it is desired to re-deposit the metal.

**Separation of Copper from Antimony.** See p. 181.

**Separation of Copper from Gold.** See p. 186.

## IRON.

### Iron from Copper.

This separation will be found on p. 154.

### Iron from Silver.

Since silver can be deposited from solutions containing excess of nitric acid, we have here a method of separation of iron from silver. As, however, the deposit of silver is not always satisfactory

from solutions containing nitric acid, and as the presence of nitrates is harmful when depositing iron, this method is hardly to be recommended. Silver is likewise readily deposited from solutions which contain potassium cyanide, but iron is not; seeing likewise that the cyanides can be afterwards decomposed by boiling with dilute sulphuric acid, the cyanide method is fairly satisfactory.

The solution containing the salts of iron and silver has about 2 or 3 grm. of potassium cyanide added to it, and the clear solution is electrolysed at a temperature of from  $50^{\circ}$  to  $60^{\circ}$ , an E.M.F. of about 2.2 to 2.5 volts being employed. The electrolytic separation of iron and silver is not of any importance.

### **Iron from Mercury.**

The separation of iron from mercury is readily carried out in solutions acidified with nitric acid (see Mercury, p. 105). Here again, however, it is necessary to remove the nitric acid or nitrates before adding ammonium oxalate or ammonium tartrate. In order to effect the removal of the nitric acid, a few cubic centimeters of sulphuric acid are added, and the solution evaporated nearly to dryness. It is then taken up with water, the excess of ammonia added, and the alkaline solution then neutralised with oxalic or tartaric acid.

Iron and mercury can likewise be satisfactorily separated in solutions acidulated with sulphuric acid. Add 1 c.c. of strong sulphuric acid to the solution, and dilute to 130 c.c. Electrolyse at a temperature of  $60^{\circ}$ , with a current of 0.4 to 0.6 ampere. In about an hour and a half the whole of the mercury will be deposited.

Mercury can be readily deposited from solutions containing excess of sodium sulphide (p. 106), whereas iron does not go into solution, but is precipitated as sulphide. This method may be made use of to separate the two metals. Excess of sodium sulphide is added to a hot neutral solution of the two metals, and the mixture is boiled for a few minutes, and then filtered. The iron sulphide is washed with a little hot water, the washings being added to the

solution of the mercury sulphide. The mercury is then electrolysed in the usual manner, care being taken that there is a sufficient excess of sodium sulphide present. The iron sulphide is dissolved in a little dilute sulphuric acid, and the solution boiled to drive off the sulphuretted hydrogen. It is then made alkaline with ammonia, and neutralised with oxalic or tartaric acid, and electrolysed as usual.

### **Iron from Zinc.**

Iron is not deposited from solutions containing free sulphuric acid, whereas zinc can be precipitated from such solutions, provided there is not a large excess of sulphuric acid present. It might therefore be supposed that there would be no difficulty in thus effecting a separation; this, however, is not the case. When a mixed solution of an iron and zinc salt containing a small quantity of sulphuric acid is electrolysed, an alloy of zinc and iron is obtained. Although this might appear to entirely invalidate the method, this is not the case, because the whole of the iron and zinc can be deposited as an alloy, and the alloy, after being weighed, is dissolved in dilute sulphuric acid. The iron goes into solution in the ferrous state, and can then be titrated with standard permanganate. The difference in the quantity of iron found and of the total weight of the alloy represents the weight of the zinc.

There are several solutions from which the alloy of zinc and iron may be deposited. Classen uses the double oxalate method.

I. The neutral solution of zinc and iron is poured into a hot solution of 8 to 10 gm. of ammonium oxalate. During the electrolysis the mixture is kept just acid by addition of small quantities of oxalic acid. The solution may be electrolysed warm with a C.D. of from 0.5 to 1 ampere.

When the electrolysis is finished, the electrode is removed, and washed and dried as usual; it is then weighed. The electrode is now placed in about 30 per cent. sulphuric acid, and the solution gently warmed, when the deposit slowly dissolves. As soon as the whole of the deposited metal has dissolved, the solution is

diluted with water, and titrated with standard potassium permanganate, the amount of iron being thus estimated.

If the amount of zinc in the original alloy is too great, there is a tendency for it to go into solution again towards the end of the reaction, and, at the same time, for hydrated oxide of iron to be precipitated.

II. The separation can also be very satisfactorily carried out from solutions containing sodium sulphate, and traces of free sulphuric acid. Here, again, if there is a large excess of zinc present, it shows a tendency to go into solution towards the end of the operation, if the precaution of adding small quantities of ammonia from time to time is omitted (p. 120). A C.D. of 0.4 to 0.8 ampere may be used, and the solution electrolysed cold.

III. Vortmann recommends the use of Rochelle salt and caustic soda: 3 or 4 grm. of Rochelle salt is added to the solution, and then an excess of 10 to 20 per cent. caustic soda solution. The mixture is then electrolysed with a low C.D. of 0.07 to 0.1 ampere. Toward the end of the electrolysis the temperature is advantageously increased to 50° or 60°. The whole of the iron is deposited in three or four hours, while the zinc remains in solution.

Hollard and Bertiaux<sup>1</sup> find, by first adding sulphurous acid to the solution of the sulphates of iron and zinc, then after nearly neutralising with sodium hydrate adding potassium cyanide, which produces potassium ferrocyanide, that only zinc is deposited.

NOTE.—In the deposition of zinc, it must be borne in mind that platinum electrodes should not be used for the reasons set out on p. 120. When an alloy is produced, and the solution has afterwards to be titrated with permanganate, the platinum should first be coated with silver, because the presence of copper would interfere with the end reaction.

### Iron from Nickel and Cobalt.

The most satisfactory way of estimating iron in presence of nickel or cobalt is again the method of alloy. Classen uses

<sup>1</sup> *Compt. Rendus*, 136, 1266.



his double oxalate method, and deposits the nickel and iron together as an alloy. The alloy is then weighed, and afterwards dissolved in sulphuric or hydrochloric acid, and the solution titrated with potassium permanganate in order to estimate the iron.

The mixed iron and nickel salt is poured into a solution of about 6 to 8 gm. of ammonium oxalate, and the mixture electrolysed at a temperature of 60° to 70°, with a C.D. of 0.5 to 1.5 ampere, the whole of the metals being deposited in the form of an alloy in from two and a half to three hours.

The alloy of iron and nickel is extremely difficult to dissolve in either dilute sulphuric or hydrochloric acids, although either acid will dissolve it if given sufficient time. Fairly concentrated warm hydrochloric acid is the best solvent, but the iron must then be titrated with  $\frac{N}{10}$  potassium dichromate.

Ammonium tartrate may be used for this separation quite as satisfactorily as ammonium oxalate, in fact the deposit often has a better appearance from this solution than from the oxalate solution.

A mixture of iron and cobalt is treated in exactly the same manner as for nickel and iron. The only difficulty is due to the red colour of the solution when titrating the iron. This red colour can, however, be neutralised by addition of small quantities of nickel sulphate to the solution, a solution of the green nickel salt and the red cobalt salt producing an almost colourless liquid.

### **Iron from Chromium.**

When a mixed solution containing iron and chromium is electrolysed after addition of ammonium oxalate or tartrate, the iron is deposited at the cathode as usual, and the whole of the chromium salt is converted into the form of a chromate. When the deposition of the iron is completed, the electrode is removed, and washed and dried as usual.

The solution now contains the chromium compound as chromate, which may be estimated by acidifying the solutions

with dilute sulphuric acid and titrating with ferrous ammonium sulphate. This estimation can be carried out either by an addition of an excess of a weighed quantity of ferrous ammonium sulphate and titrating back with potassium permanganate—the end reaction, however, is rather difficult to see; or by titrating with a standard solution of ferrous ammonium sulphate, using potassium ferricyanide as an indicator.

Another method is to acidify the solution with sulphuric acid and reduce the chromate with sulphurous acid; or reduce by acidifying with hydrochloric acid and boiling with alcohol. The chromium in the reduced solution is then precipitated as hydroxide by addition of ammonia, and the hydroxide is filtered off, washed, dried, and ignited, the chromium being estimated as  $\text{Cr}_2\text{O}_3$ .

### **Iron from Aluminium.**

A method somewhat similar to that employed in separating iron from chromium may be employed for separating iron and aluminium. Excess of ammonium oxalate or tartrate, about 8 to 10 grm., is added to the neutral solution of the mixed metals, and the solution electrolysed as usual.

At the commencement of the electrolysis only iron is deposited, but as the quantity of iron decreases, and ammonium carbonate is produced by the decomposition of the ammonium oxalate, small quantities of aluminium hydroxide may be deposited as white gelatinous flakes. If the quantity of aluminium hydroxide thus deposited is only small, it can be neglected. But when a considerable amount is thrown out, it has a tendency to adhere to the negative electrode, and is then rather difficult to remove; this causes the weight of iron to appear too high, and that of the aluminium too low. In this case it is best to add a slight excess of oxalic acid, in order to bring the hydroxide into solution again; on further electrolysis, the whole of the iron is thrown out. The aluminium in the solution is estimated by addition of excess of ammonium hydrate, whereby the aluminium is precipitated as hydroxide, and is then estimated in the usual manner as  $\text{Al}_2\text{O}_3$ .

When ammonium tartrate is used as electrolyte, the aluminium hydroxide is not precipitated, therefore it is to be recommended rather than the oxalate. In this latter case, the C.D. should not exceed 1 ampere, but is better to be kept at 0.8 of an ampere.

According to Hollard and Bertiaux,<sup>1</sup> the addition of sulphurous acid to the electrolyte prevents the deposition of aluminium hydroxide, when oxalate solutions of aluminium and iron are electrolysed.

## Iron and Manganese.

As iron and manganese are constantly met occurring together, and as the ordinary methods of separation of these two metals are not very satisfactory, a good electrolytic method would be of great importance. Owing to these causes a great many attempts to obtain a satisfactory separation have been made, but it is only quite recently that a successful process has been devised. It might be supposed, seeing that manganese can readily be deposited at the anode, but that iron is always precipitated on the cathode, that there should be no difficulty in devising a separation. But unfortunately there is a great tendency on the part of the iron to be deposited in greater or less quantities as hydrated oxide along with the manganese oxide.

Classen has recommended his oxalate method for separating iron and manganese, but there is here always a tendency for a mixture of ferric hydrate to be deposited along with the manganese hydrate at the anode.

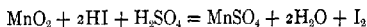
A. Hollard and Bertiaux<sup>2</sup> find that the addition of sulphurous acid prevents the precipitation of the iron oxide. The electrolyte consists of a mixture of ammonium citrate and ammonium sulphate, about 3 to 4 grm. of each. The solution is electrolysed with a C.D. of 1 ampere, and at a temperature of 48°. It is found that the iron is deposited more rapidly than the manganese, therefore the larger electrode, *e.g.* the basin or flag, is made the cathode.

<sup>1</sup> *Compt. Rendus*, 1903, **136**, 1266.

<sup>2</sup> *Ibid.*, 1903, **136**, 1266.

As soon as all the iron has been deposited, the cathode is removed, the iron dissolved in dilute sulphuric acid, and titrated with potassium permanganate. A certain amount of the cathode deposit may consist of iron sulphide, and when this is dissolved, sulphuretted hydrogen is evolved. It is necessary, of course, to make sure this has all been driven off before titrating with permanganate.

The larger electrode is now made the anode, the smaller previous anode coated with some of the peroxide being now the cathode. This coating of peroxide passes into solution, and, together with the manganese remaining in the original solution, is deposited upon the anode. The temperature employed for this latter electrolysis is  $90^{\circ}$  to  $95^{\circ}$ . The amount of the deposited manganese is determined by ascertaining how much iodine is liberated by it from an acid solution of potassium iodide.



When a solution containing iron and manganese, to which has been added an excess of ammonium oxalate, is electrolysed, the iron commences to come down before the manganese, and it is only after some little time that the manganese peroxide commences to separate. As soon as the manganese begins to separate, J. Kuster<sup>1</sup> finds that the addition of small quantities of phosphorous acid, added from time to time during the first two hours of the electrolysis, prevents the deposition of ferric hydrate, and likewise prevents the precipitation of manganese peroxide.

The solution is electrolysed with a C.D. of 1.5 to 2 amperes at ordinary temperatures, and as soon as the manganese commences to be deposited at the anode, 1 or 2 c.c. of a 10-per-cent. solution of phosphorous acid is added. The manganese deposit immediately vanishes, and the solution becomes reddish. As more manganese is thrown out, a further quantity of phosphorous acid is added. After about 2 hours, when the main portion of iron has been deposited, it is no longer necessary to add any more phosphorous acid. The addition of about 15 c.c. of phosphorous

<sup>1</sup> *Ber.*, 1903, 36, 2716.

acid at the commencement of the operation entirely prevents the deposition of manganese peroxide. Too much phosphorous acid should not be added, because this causes the iron to be precipitated very slowly. The whole of the iron is deposited in from five to ten hours, depending upon the amount of phosphorous acid added. Toward the end of the reaction the solution becomes dark brown in colour, and may be opaque from the presence of more or less precipitated hydrated oxide of manganese. On dilution with water the hydroxide is thrown out.

### **Iron from Lead.**

Iron can readily be separated from lead by electrolysing in a solution containing excess of nitric acid. The lead is deposited at the anode as peroxide, and the iron remains in solution. Before depositing the iron, it is necessary to get rid of the nitric acid. The best way is to precipitate the iron as ferric hydrate by the addition of excess of ammonia; the precipitate is then well washed with hot water and dissolved in oxalic acid, and the oxalic acid solution neutralised with ammonia. Or the ferric hydrate may be dissolved in tartaric acid, the solution exactly neutralised with ammonia, and the iron deposited as usual.

### **COBALT AND NICKEL.**

Many attempts have been made to separate cobalt and nickel electrolytically, but none of the methods so far published can be said to give very satisfactory results. The only method which can be at all recommended is that of A. Coehn and M. Gläser,<sup>1</sup> and even this cannot be termed absolutely quantitative, but probably with a little alteration it might be improved.

The process depends upon the simultaneous deposition of the two metals—nickel at the cathode and cobalt at the anode. In order to deposit cobalt quantitatively at the anode, naturally the metal must, by some means or other, be prevented from being

<sup>1</sup> *Zeit. f. Anorg. Chem.*, **33**, 9.

precipitated on the cathode. Now, as hydrogen is only deposited 0.22 volts higher than cobalt, too high an E.M.F. must not be employed, or else one must employ some method in which the deposition takes place at a lower potential than that at which the H ions are discharged, *e.g.* the addition of a chromate to the solution. The method employed by Coehn and Gläser is as follows :—

To the neutral solution, which should not contain more than 0.1 gm. of cobalt, 0.1 to 0.2 gm.  $K_2Cr_2O_7$  is added, and 3 to 4 gm. potassium sulphate. The solution which is made up to 500 c.c. is electrolysed with an E.M.F. of 2.3 to 2.4 volts, the current being about 0.10 to 0.15 ampere. In about ten hours the whole of the cobalt is deposited as peroxide, and the nickel as metal on the cathode. The cobalt oxide deposit is afterwards dissolved in acid, and after neutralisation deposited in the usual manner in the metallic form on the cathode.

**Cobalt and Nickel from Iron.**—See p. 165.

### **Cobalt and Nickel from Copper.**

The solution containing the cobalt and copper salts or a mixture of all these is electrolysed in a solution containing an excess of nitric acid. Copper only is deposited on the cathode, the nickel and cobalt remaining in solution.

As both nickel and cobalt are only deposited with difficulty from solutions containing nitric acid or nitrates, the solution remaining after the copper has been deposited must be evaporated to small bulk with sulphuric acid in order to drive off the nitric acid. The cobalt or nickel are then analysed in the usual manner.

### **Cobalt and Nickel from Silver.**

Two methods may be used to effect the separation of nickel or cobalt from silver. Either a solution acidified with nitric acid can be employed, or a solution containing the double cyanides

of these metals. Solutions of the double cyanide are preferable. The E.M.F. is kept as low as possible, a current of 0.1 ampere being employed, but however much care is taken, there is always a tendency for the silver and nickel to be deposited together. Seeing with what great ease silver can be separated from cobalt and nickel by ordinary chemical means, it is obvious that there is no advantage to be obtained by employing the somewhat doubtful electrolytic method.

### **Cobalt and Nickel from Zinc.**

The mixed salts are dissolved in water, and then poured into a solution of from 5 to 6 grm. of rochelle salt (potassium sodium tartrate) and then excess of sodium hydrate added, after which the solution is made up to the required bulk. A current of from 0.3 to 0.6 ampere may be used. The zinc is deposited, but the nickel and cobalt remain in solution, the whole of the zinc is deposited in from three to four hours. With cobalt salts there is a tendency for part of the cobalt to be deposited at the anode as oxide; if this should be noticed, the addition of small quantities of hydroxylamin sulphate or chloride from time to time will cause it to dissolve off, or a small quantity of potassium iodide may be added. There is a marked tendency for the zinc to be deposited in a spongy form, and to be very burnt in appearance.

### **Cobalt and Nickel from Lead.**

This separation is readily carried out in solutions containing excess of nitric acid. The cobalt and nickel are not deposited, but the lead is precipitated as peroxide on the anode. A current of 1 to 1.5 amperes may be employed, and the solution is best electrolysed at 60° to 70°. If it is afterwards desired to deposit the nickel or cobalt, the nitric acid must first be got rid of, because in presence of nitrates the metals are thrown out exceedingly slowly, although the deposits are often extremely good.

### **Cobalt and Nickel from Manganese.**

The separation of nickel or cobalt from manganese may be carried out in a similar manner to that described for separating iron and manganese. The method can, however, hardly be recommended as being one of any great degree of accuracy (see p. 168).

### **Nickel and Cobalt from Mercury.**

This separation can be carried out in solutions containing free nitric or sulphuric acid. Owing to the fact that nickel and cobalt are only slowly deposited from solutions containing nitrates, it is better in this case to use solutions containing about 3 per cent. of sulphuric acid. The electrolysis may either be conducted at ordinary temperatures or at a temperature of  $55^{\circ}$  to  $70^{\circ}$ ; the ordinary precautions adopted in depositing mercury must be observed (see p. 104).

Beside employing acid solutions, solutions containing potassium cyanide may be used; from the latter solution, nickel and cobalt are only deposited with currents of a considerable E.M.F., whereas mercury can be deposited readily with currents of low potential, from about 1.5 volts. It is best to electrolyse at a temperature of from  $55^{\circ}$  to  $70^{\circ}$ ; the presence of cobalt causes the mercury to be deposited more slowly. Generally speaking, about 0.3 gm. of mercury can be deposited in about three hours, but it may require from four to five hours. The E.M.F. should not rise above 1.9 volts.

## **MERCURY.**

The separation of mercury from the other metals can be carried out on much the same lines as the methods adopted for separating silver from other metals.

**Separation of Mercury from Copper.**—See p. 160.

**Separation of Mercury from Iron.**—See p. 163.



**Separation of Mercury from Cobalt and Nickel.—**

See p. 173.

**Mercury from Lead.<sup>1</sup>**

It might be supposed that mercury and lead could be very readily separated by electrolytical methods, in solutions containing nitric acid, the mercury being deposited on the cathode, and the lead as peroxide at the anode. To a considerable extent this does take place; but if less than 15 per cent. of nitric acid be present, the lead is only partially deposited at the anode, a portion coming down as metal at the cathode and forming an amalgam with the mercury. If low currents are employed, this combined deposition at the cathode can be almost completely prevented. The C.D. should not be above 0.2 ampere, and there should be from 25 to 30 c.c. of nitric acid (sp. gr. 1.3) added for every 150 c.c. of solution.

**Mercury from Manganese.**

From solutions containing free sulphuric acid and a small quantity of chrome alum, mercury and manganese can be separated, the manganese being deposited on the anode as oxide, and the mercury on the cathode. The smaller electrode must be used as cathode; for the rest, it is only necessary to use the conditions and precautions necessary for depositing manganese, in order to obtain a complete separation (see p. 138).

**Mercury from Silver and Gold.**

It is not possible to directly separate mercury from silver and gold by electrolytic means, as the decomposition values of the salts of these three metals lie too closely together. But mercury and silver or mercury and gold can readily be obtained as amalgams, either from solutions containing free nitric acid or from cyanide solutions.

<sup>1</sup> Smith and Moyer, *Zeit. f. Anorg. Chem.*, 4, 267. Heidenreich, *Ber.*, 29, 1585.

The C.D. may vary from 0.1 to 0.7 amperes. When the mercury and silver or mercury and gold have been deposited, the amalgam is weighed, and then the mercury driven off by heating; on cooling and again weighing, the loss of weight represents the amount of mercury which had been deposited. Care must be taken not to heat the amalgam to too high a temperature, or there will be a danger of causing the silver or gold to alloy with the platinum electrode. In order to make quite sure that the whole of the mercury has been driven off, the electrode should be again heated, and, if any loss in weight is noticed, it must be heated until a constant weight is obtained.

### **Mercury from Antimony.**

When a solution containing a mixture of mercury and antimony salts is electrolysed with a current of from 0.015 to 0.09 ampere and an E.M.F. of 2.0 to 3.6 volts, the whole of the mercury is deposited, while the antimony remains in solution. About 5 grm. of tartaric acid and 15 to 20 c.c. of 10-per-cent. ammonia is added to the solution to be electrolysed, which, after heating to 50° or 60°, is electrolysed with the currents above stated; the antimony must be present in the higher state of oxidation. The deposition requires about six or seven hours. After all the mercury has been deposited, the antimony can either be deposited from the same solution by rendering it quite neutral, and passing a current of from 0.5 to 0.8 ampere—the electrolysis is best conducted at ordinary temperatures; or the antimony can be precipitated with sulphuretted hydrogen, dissolved in excess of sodium sulphide, and electrolysed as described on p. 108.

### **Mercury from Arsenic.**

Mercury can readily be separated from arsenic, from solutions containing free nitric acid; about 1 to 3 per cent. is sufficient. The E.M.F. should not exceed 1.8 volts; the mercury is deposited, and the arsenic remains in solution. When high currents are employed, the deposited mercury is contaminated with arsenic.

### Mercury from Tin.

Mercury can be separated from tin in an exactly similar manner to that employed in separating it from antimony, namely, from solutions containing tartaric acid and ammonium tartrate. The mercury salt should first be added to the tartaric acid, and then the ammonia mixed with it, after which the tin salt may be added, and the mixture electrolysed at a temperature of  $55^{\circ}$ , the potential not being allowed to exceed 1.7 volts.

Mercury can also be separated from tin by taking advantage of the fact that, although mercury can be deposited from solutions containing a large excess of sodium sulphide, tin is not precipitated from such solutions by the electric current. About 20 to 30 c.c. of a concentrated solution of sodium sulphide is added to the mixture of mercury and tin, and the solution diluted to 125 or 130 c.c.

This mixture is then electrolysed with a current of from 0.1 to 0.15 ampere, the temperature being about  $70^{\circ}$ ; under these conditions the E.M.F. will be about 2.5 volts. In about five or six hours the whole of the mercury will have been deposited.

### SILVER.

Separation of Silver from Copper.—See p. 157.

Separation of Silver from Iron.—See p. 162.

Separation of Silver from Nickel and Cobalt.—See p. 171.

Separation of Silver from Mercury.—See p. 174.

### Silver from Cadmium.

From Cyanide Solution.—About 2 grm. of potassium cyanide—which must be pure, otherwise the silver deposit may be brown in colour—is added to the solution containing the cadmium and silver salts, and the solution diluted to about 130 c.c. With low currents of 0.02 to 0.03 ampere, and at a temperature of

60° to 80°, the whole of the silver will be deposited, while the cadmium will remain in solution. The E.M.F. will be about 2.1 volts; from five to six hours will be required to deposit 0.1 to 0.2 gm. of silver.

The cadmium can either be deposited from the cyanide solution by increasing the current to 0.5 or 0.8 ampere, or the cyanide can be decomposed, and one of the other methods described under Cadmium (p. 114) may be employed for its deposition.

**From Nitric Acid Solution.**—To the solution of the mixed salts add 10 to 12 c.c. of nitric acid (sp. gr. 1.4), and make up to 130 or 140 c.c. Heat to 60° or 65°, and electrolyse with a low current, so that the E.M.F. shall not exceed 2.0 to 2.8 volts. The silver may in this case be deposited in a more or less crystalline form, and probably will not adhere very well to the electrode.

The cadmium remains in solution, and can be deposited by adding excess of sodium or ammonium acetate to neutralise the nitric acid, and then electrolysing with a current of 0.1 to 0.2 ampere.

### **Silver from Lead.**

Add 8 c.c. concentrated nitric acid to the solution containing the mixture of lead and silver salts, and then make up to about 150 c.c. Electrolyse at a temperature of 80°, with a current of 0.18 to 0.2 ampere. The silver and lead are deposited simultaneously—the silver on the cathode, the lead on the anode as peroxide. The usual precautions as to washing and drying the deposits, necessary for silver and lead, are adopted.

For the estimation of small quantities of silver in presence of large amounts of lead, see p. 189.

### **Silver from Tin.**

The separation of silver from tin is best carried out by a combination of chemical and electrolytical methods, and may be done as follows:—

Pass sulphuretted hydrogen into the acid solution containing the tin and silver salts. Filter off the mixed sulphides, well wash with water, and then treat with successive small quantities of ammonium sulphide.

The tin sulphide dissolves, and the solution so obtained, after dilution to the requisite volume, is electrolysed hot, with a current of 0.5 to 1 ampere, the usual precautions necessary to electrolysing tin being followed. (See p. 112.)

The silver sulphide is washed with water and dissolved in a solution of potassium cyanide, or dissolved in warm nitric acid, evaporated to small bulk to drive off excess of nitric acid, neutralised with ammonia and treated with potassium cyanide. It is then electrolysed as described on p. 121.

### Silver from Antimony.

The separation of silver from antimony is similar to that employed for separating it from tin. The mixed sulphides are treated with ammonium sulphide, or better with sodium sulphide, and the antimony solution so obtained electrolysed as usual; the silver, after treatment with potassium cyanide, electrolysed *per se*.

Silver and antimony can also be separated by purely electrolytical methods, and these are extremely exact when carried out with care. According to A. Fischer,<sup>1</sup> the metals can be separated from a solution in nitric acid in the following manner:—

I. To a solution of the antimony and silver salt, the total volume of which is 160 c.c., 5 grm. of tartaric acid and 2 c.c. of nitric acid (sp. gr. 1.4) are added. This solution is electrolysed in the cold with an E.M.F. of 1.3 to 1.5 volt, the current varying from 0.01 to 0.05 ampere. Under these conditions the time required is about eighteen hours. But at a temperature of 50° to 60°, with the same E.M.F., the current is 0.02 to 0.12 ampere, and the whole of the silver is deposited in eight to nine hours.

When the whole of the silver has been deposited out, the solution is evaporated to small bulk, made alkaline with sodium

<sup>1</sup> Ber., 36, 3345.

hydrate, and about 80 c.c. of sodium sulphide added. If the solution is yellow, potassium cyanide may be added until it becomes colourless. The antimony is then deposited from this solution in the usual manner (p. 108).

II. The separation can also be carried out from solutions containing potassium cyanide and tartaric acid; the addition of tartaric acid is necessary to cause the solution of the antimony salt. The electrolysis can either be conducted at the ordinary temperature, when eighteen hours are required to deposit all the silver, or at 30° to 50°, when eight hours are sufficient.

**Procedure.**—Add to the solution a solution of from 3 to 5 gm. potassium cyanide and 0.5 to 1 gm. of tartaric acid: the mixture is then made up to 150 to 160 c.c., and electrolysed with an E.M.F. of 2.0 to 2.4 volts. The antimony, when in the pentad condition, is not deposited unless the E.M.F. rises above 2.6 volts; but when it is in the lower state of oxidation it begins to be reduced at 2.0 to 2.1 volts; therefore, in order to separate the two metals in potassium cyanide solution, the antimony must be in the pentad condition.

It is important that the potassium cyanide employed should be of the purest, otherwise the solution becomes brown, and polymerisation products of hydrocyanic acid may be deposited upon the silver, and lead to incorrect results.

When the whole of the silver has been deposited, the solution is evaporated to small bulk, and 70 to 80 c.c. of sodium sulphide added; the antimony is then deposited as usual.

### **Silver from Zinc.**

Both zinc and silver can be deposited from cyanide solutions, but the silver can be deposited at a much lower potential than the zinc. If, therefore, a low current density is employed, the E.M.F. obtained is not sufficient to deposit the zinc; while it is quite high enough to decompose the silver solution. With a current density of 0.025 to 0.035, the E.M.F. is about 2.65 to 2.75 volts; in about three or four hours the whole of the silver will be deposited.

Since the deposition of zinc from cyanide solutions is extremely slow and rather uncertain, it is best to decompose the cyanide by warming with small quantities of sulphuric acid, and, after nearly neutralising the excess of sulphuric acid with ammonium hydrate, electrolysing with a C.D. of 0.03 to 0.06 ampere. The whole of the zinc will be deposited in about two or three hours. For the precautions necessary when depositing zinc from sulphuric acid solutions, see p. 120.

## LEAD.

Separation of Lead from Copper.—See p. 161.

Separation of Lead from Iron.—See p. 170.

Separation of Lead from Cobalt and Nickel.—See p. 172.

Separation of Lead from Mercury.—See p. 174.

Separation of Lead from Silver.—See p. 177.

## Separation of Lead from Antimony.

Antimony and lead are often found together in alloys, therefore a good method of separating these metals would be extremely useful. Neumann and Nissenson<sup>1</sup> recommend dissolving the alloy (2.5 gm.) in a warm mixture of 10 gm. of tartaric acid, 15 c.c. water, and 4 c.c. nitric acid (sp. gr. 1.4). A clear solution can thus be obtained, and to this is added 4 c.c. of concentrated sulphuric acid; on cooling, the solution is made up to 250 c.c. The precipitated lead sulphate is then filtered off, and, in order to determine the antimony, 50 c.c. of the filtrate is made strongly alkaline with caustic soda, and 50 c.c. of a strong solution of sodium sulphide added. The mixture is then warmed, and, if necessary, it is filtered, and the clear solution electrolysed for antimony as usual with a current density of 1.5 to 1.75 amperes. (See p. 108.)

<sup>1</sup> Neumann and Nissenson, *Chem. Zeit.*, 1895, 49.

If it is desired to estimate the lead, the lead sulphate is digested with a little concentrated ammonium hydrate for a few minutes. The lead sulphate is thereby converted into hydrate, then it is cautiously washed into a solution of 20 c.c. nitric acid. After making up to the required bulk, the solution is electrolysed as usual (p. 137).

## ANTIMONY.

Separation of Antimony from Silver.—See p. 178.

Separation of Antimony from Mercury.—See p. 175.

### Antimony from Copper.

Copper may be separated from antimony in solutions containing tartrates, the copper being deposited, the antimony remaining in solution.<sup>1</sup> To a solution containing about 0.1 gm. of the two metals add 8 gm. of tartaric acid and 25 c.c. of strong ammonia. It is necessary for the antimony to be present in the pentad condition. Heat the mixture to 50°, and electrolyse with a current density of 0.08 to 0.10 ampere; the E.M.F. will be about 1.8 to 2.0 volts. The whole of the copper is deposited in from five to six hours. The antimony can then be deposited, by making the solution exactly neutral with tartaric acid, and electrolysing the hot solution with a current of 0.2 to 0.5 ampere. (See p. 111.)

### Antimony from Tin.<sup>2</sup>

While tin can be quantitatively deposited from solutions containing excess of ammonium sulphide, it cannot be obtained quantitatively from solutions to which has been added sodium sulphide; in fact, if sufficient excess of sodium sulphide is present, the precipitation of the tin by the electric current is entirely prevented.

<sup>1</sup> *Journ. Amer. Chem. Soc.*, **15**, 195, and *Zeit. f. Anorg. Chem.*, **4**, 274.

<sup>2</sup> *Ber.*, XVII. 2245; XVIII. 1110 and 2060.



The sodium sulphide should be as pure as possible; for this reason it is best to employ the solution prepared as described on p. 282. When the article of commerce is employed—which always contains free caustic alkali and other impurities—a concentrated solution should be prepared and saturated with sulphuretted hydrogen gas. The solution is then boiled and filtered, and finally evaporated until, when cold, it commences to crystallise.

In order to carry out the separation, 70 to 80 c.c. of the concentrated solution of sodium sulphide is added to the sulphides of the two metals. The tin, if not already in the stannic condition, must be converted into the higher state of oxidation by the addition of hydrogen peroxide before adding the sodium sulphide. If the metals are obtained in acid solution, sufficient sodium hydrate is added to make the mixture just alkaline—a precipitation of the hydrates of tin or antimony does not matter—and the sodium sulphide is added. In any case, after the addition of the sodium sulphide 1 to 2 grm. of sodium hydrate is added; this must be of sufficient purity not to give a precipitate with sulphuretted hydrogen.

The solution may either be electrolysed at ordinary temperatures or at a temperature of 50° to 60°.

#### CONDITIONS.

C.D. . . . .	0.2 to 0.9 ampere.
E.M.F. . . . .	0.9 to 1.2 volts.
Time. . . . .	2 to 15 hours, depending upon the temperature and C.D. At temperatures of 50° to 60° and with 0.5 ampere C.D. between 2 and 3 hours are required.

At the commencement of the reaction the solution often becomes opaque from the gassing which takes place, but toward the end of the process the solution becomes quite clear. When the whole of the antimony has been deposited, the electrodes are removed, and the cathode is rapidly washed and dried.

The tin cannot be deposited from solutions containing sodium sulphide; it is therefore necessary to convert the sodium sulphide into ammonium sulphide. This can be done by adding about 25 grm. of ammonium sulphate and warming until the evolution

of hydrogen sulphide ceases, after which boil for ten to fifteen minutes. Cool, and, if any sodium sulphate separates out, add sufficient water to dissolve this. The tin can now be deposited by electrolysing with a C.D. of 0.3 to 0.5 ampere, either at the normal temperature or at 30°.

Another method is to precipitate the sulphide of tin by acidifying with dilute hydrochloric acid; this can then be filtered off, and, after washing, be dissolved in ammonium sulphide. As, however, stannic sulphide is rather difficult to filter, it is better to employ the first method.

Classen prefers to convert the thioannate into the oxalate, and, as tin deposits very well from solutions of the double oxalate, the method may be recommended. In order to do this, the thiosalts are partly decomposed with sulphuric acid—the solution must not be made acid. On warming, the major portion of the thiosalts are decomposed, and hydrogen sulphide is driven off. Hydrogen peroxide is now added until the metastannic acid precipitated becomes quite white. The mixture is now acidulated with sulphuric acid, neutralised with ammonia, a further quantity of hydrogen peroxide added, and the mixture boiled until all the peroxide is decomposed, as shown by effervescence ceasing.

The stannic acid is then filtered off and dissolved in oxalic acid; then, after addition of 3 or 4 grms. of ammonium oxalate, the solution is electrolysed with a C.D. of 0.2 to 0.3 ampere. The time required will be about eight or nine hours.

Tartaric acid and ammonium tartrate may be substituted for the oxalic acid and ammonium oxalate.

A. Fischer<sup>1</sup> and also A. Hollard<sup>2</sup> find that the separation of tin and antimony can be carried out when small quantities of potassium cyanide are present. The sulphides of the two metals are dissolved as usual in sodium sulphide, and potassium cyanide solution is added drop by drop until the solution is quite colourless; it is then electrolysed with an E.M.F., which must not exceed 1.1 volt, and at a temperature of 30°. The tin which remains in solution is then worked up as usual.

<sup>1</sup> *Ber.*, **36**, 2348.

<sup>2</sup> *Bull. Soc. Chim.*, **20**, 262.

## ARSENIC.

In separating arsenic from solutions containing other metals, it is never attempted to deposit out the arsenic; but conditions are sought which will allow the deposition of the other metal, while the arsenic remains in solution and can afterwards be estimated by chemical means. Generally speaking, when arsenic is present, it is necessary to employ a lower C.D. in depositing the other metal than is otherwise the case.

### Copper from Arsenic.

I. **From Solutions containing Potassium Cyanide.**—To the solution containing arsenic and copper add potassium cyanide until the precipitate first formed is just dissolved. Electrolyse at a temperature of  $60^{\circ}$  with a C.D. of from 0.20 to 0.25 ampere; the E.M.F. will be 3.3 to 3.6 volts. The whole of the copper can usually be deposited in from 3 to 3.5 hours.

II. **Nitric Acid Solution.**—Add about 5 c.c. of concentrated nitric acid to every 100 c.c. of solution, and electrolyse at a temperature of  $50^{\circ}$  to  $60^{\circ}$ , taking care not to allow the E.M.F. to exceed 1.9 volts. Or the deposition may be carried out in the cold overnight. According to Hollard and Bertiaux, the addition of small quantities of ferric sulphate prevents the deposition of the arsenic, the arsenic thereby being kept in the higher state of oxidation.<sup>1</sup>

### Antimony from Arsenic.

Treat the alloy or compound (about 1 grm.) containing arsenic and antimony with aqua regia, and evaporate to dryness. Add a few cubic centimeters of water to the residue, and from 2 to 3 grm. of sodium hydrate; then add 70 or 80 c.c. of a concentrated solution of sodium hydrate and 1 grm. of potassium cyanide, dilute to the required volume, and electrolyse at a temperature of  $30^{\circ}$  or  $40^{\circ}$ .

#### CONDITIONS.

C.D. . . . . 1.3 to 1.5 ampere.

E.M.F. . . . . 2.3, reducing towards the end to 1.5 volts.

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<sup>1</sup> *Bull. Soc. Chim.*, 1904, [iii.] 81, 900.

In about 6 or 7 hours the whole of the antimony will have been deposited. The arsenic remains in solution, and may be estimated by ordinary chemical means.

If metals of the copper group are present, they must be separated chemically before the antimony is deposited, in which case the antimony and arsenic will be obtained in the form of their sulphides, and can then be directly dissolved in 70 c.c. of sodium sulphide.

### ANALYSIS OF ALLOYS.

#### **Sterling Silver.**

Sterling silver is an alloy consisting of silver and copper.

The British silver coin contains silver 92.5 per cent.

The United States silver coin contains silver 90 per cent.

The German       "       "       "       90       "

The French       "       "       "       83.5 to 90 per cent.

The analysis of this alloy is comparatively simple, but it requires care when conducted upon purely electrolytical lines. The simplest method is to dissolve the coin in nitric acid, and precipitate the silver as chloride. The silver can then be weighed as chloride or dissolved in potassium cyanide and electrolysed. The solution containing the copper must then be evaporated nearly to dryness, in order to expel the excess of hydrochloric acid, then taken up with water and nitric acid, and the electrolysis conducted as usual (see p. 86). If the separation is to be carried out entirely with the electric current, then the two metals can be separated either from solutions containing free nitric acid (see p. 160), or, better, from solutions containing potassium cyanide (see p. 159).

#### **Bronze—Copper Coinage.**

From 0.2 to 0.4 gm. of the alloy in the form of turnings or filings is dissolved in nitric acid. It is best to first cover the alloy with strong nitric acid (sp. gr. 1.5), and then add water drop by drop until a vigorous reaction sets in. When the whole of the

alloy has dissolved, the solution is diluted with water and boiled, and the precipitated oxide of tin filtered off and thoroughly washed, the washings being returned to the original solution.

The simplest procedure with reference to the tin is to weigh it directly as oxide, or it can be boiled up with ammonium sulphide solution, and analysed electrolytically from this solution. (See p. 112.)

The filtrate containing the copper and zinc and excess of free nitric acid is electrolysed directly. The copper is deposited on the cathode, the zinc remaining in solution. (See p. 86.)

Before proceeding to estimate the zinc, the nitric acid should be removed, after which the zinc may be estimated from an oxalate (p. 119) or acetate (p. 120) solution. Bronze coinage in Great Britain contains :—

Copper . . . . .	95 parts.
Zinc . . . . .	1 part.
Tin . . . . .	4 parts.

**Bell metal** contains 3 parts copper and 1 part tin; **speculum metal** 1 part tin and 2 parts copper; but these alloys vary to some extent. **Gun metal** contains about 90 parts copper and 10 parts tin.

Bronzes sometimes contain small quantities of lead, in which case the lead is deposited on the anode as peroxide when electrolysing the solution for copper. They also frequently contain traces of iron.

### **Copper and Gold—Sterling Gold.**

Sterling gold used in making the British coinage contains 91·66 per cent. gold, the rest being copper. The alloy employed for making the German gold coinage contains 90 per cent. of gold and 10 per cent. of copper. Pure gold is said to be 24 carats. Sterling gold is 22 carats. Gold of 18 carats contains 18 parts of gold and 6 parts of copper or some other metal alloyed with it; and 15 carat gold consists of 15 parts of gold and 9 parts of some other metal, usually copper or silver.

In order to analyse an alloy of gold and silver, the material is dissolved in aqua regia, and evaporated to dryness. The residue is then taken up with a little dilute hydrochloric acid, a slight excess of sodium hydrate is added, and about 4 gm. of potassium cyanide. The solution is then electrolysed with a C.D. 0.05 to 0.08 ampere; the potential should not be allowed to exceed 2 volts. The solution should be electrolysed at a temperature of 60° to 65°. The whole of the gold can at this temperature be deposited in about three hours.

The copper can be deposited from the cyanide solution by decomposing a portion of the cyanide with dilute nitric acid, and electrolysing with a current density of 0.5 to 1 ampere.

### **Alloys of Copper and Nickel— Nickel Coinage.**

The alloy is dissolved in nitric acid, which should be fairly dilute. The solution is then made up to the required volume, and about 3 or 4 c.c. of concentrated nitric acid added. It is now electrolysed for copper as usual.

After all the copper has been removed, the solution is evaporated nearly to dryness with a little sulphuric acid, in order to drive off the excess of nitric acid, diluted with water, and 3 gm. of ammonium borate and 30 c.c. of strong ammonia added. The solution is electrolysed as usual for nickel. (See p. 95.)

It generally happens that small quantities of iron are present in the alloy; the iron, if any, is precipitated as hydrate when the ammonia is added. It should be filtered off before proceeding to determine the nickel.

The ferric hydrate can be dissolved in oxalic acid or tartaric acid, and, after neutralisation with ammonia, estimated electrolytically as usual. (See p. 101.)

The German nickel coin consists of copper 75 per cent., and nickel 25 per cent. The nickel coin used in the United States contains the same quantities of nickel and copper as the German coin.

### **Copper, Zinc, and Nickel—German Silver.**

The metal is dissolved in nitric acid, and the copper deposited out as in the separation of copper from nickel.

The solution, which now contains the zinc and nickel, is evaporated to small bulk with sulphuric acid, in order to expel the excess of nitric acid. From this solution either the nickel can be deposited first—the zinc remaining in solution—or the zinc can first be thrown out, leaving behind the nickel.

**Deposition of the Zinc.**—Five to six grm. of Rochelle salt, sodium potassium tartrate, is added to the solution, and then a considerable excess of caustic soda. A current of 0.3 to 0.5 ampere is then passed through the solution, which is kept at ordinary temperatures. In from three to four hours, the whole of the zinc will have been deposited. If there is a tendency for nickel oxide to separate at the anode, about 0.2 to 0.5 grm. of hydroxylamine hydrochloride may be added; this causes the oxide to pass into solution again.

As soon as the whole of the zinc has been deposited, which may be determined by hanging a piece of copper wire over the cathode, the solution is, after the removal of the cathode, acidified with sulphuric acid, then made strongly alkaline with ammonia, and the nickel determined as usual. (See p. 92.)

**Deposition of the Nickel.**—Von Foregger finds that it is possible to deposit the whole of the nickel first, while the zinc remains in solution. To the solution which remains, after the copper has been deposited, and from which the excess of nitric acid has been driven off, 10 grm. of ammonium carbonate and 10 c.c. ammonium hydrate (sp. gr. 0.880) are added. The solution is then diluted to 150 c.c., and electrolysed with a C.D. of 0.3 to 0.5 ampere, which toward the end is increased to 1 ampere. The temperature of the electrolyte is maintained at 55° to 60°.

When the whole of the nickel has been deposited, which can be ascertained by the addition of ammonium sulphide to a small

quantity of the solution, the cathode is removed and weighed. The zinc which remains in solution can be deposited by making the solution slightly acid with oxalic acid, and electrolysing as usual when determining zinc in oxalate solutions (p. 119).

### **Commercial Lead for Traces of Silver.**

Arth and Nicholas<sup>1</sup> have determined the most favourable conditions for estimating small quantities of silver in presence of large amounts of lead.

In solutions containing sufficient acid, lead is not deposited on the cathode in the metallic form, and only at the anode as peroxide, when a large amount of free acid is present. In order to deposit metallic lead, the E.M.F. required is fairly high, and the amount of free acid employed must be considerable.

Silver only requires moderately acid solutions, and a low E.M.F.; but, as already mentioned, silver is very apt to be deposited in a crystalline or spongy non-adherent form from acid solutions. Kuster and Steinwehr have shown that this difficulty can be surmounted by using an E.M.F. which does not exceed 1.38 volts. Bearing these facts in mind, the authors found with 1.2 volts that a spongy deposit of lead began to form along with the silver. With 1.1 volt this was not the case.

In order not to exceed a pressure of 1.1 volt, they find it best to employ a source of current which on the open circuit does not exceed 1.1 volt. The minimum concentration of acid is 1 per cent. by volume; 6 c.c. of alcohol is also added. With a larger quantity of acid, lead may be deposited. At ordinary temperatures the deposition of silver is incomplete, and adheres badly; therefore the electrolysis must be carried out at a temperature of 60°.

This method has been employed for the detection and estimation of silver in ordinary sheet lead. For example, in one case in 100 gm. of lead, 0.0042 gm. silver was obtained, or 1 part

<sup>1</sup> *Bull. Soc. Chim.*, **XXIX**, 13.



in 23,809; in another case, 1 part in 75,000 parts of lead was found and estimated.

In dealing with such large quantities of lead, the bulk of solution will have to be very considerable, and the solution should be kept agitated, if not continuously, at any rate, from time to time.

### **Antimony, Arsenic, and Tin—Britannia Metal.**

The metal is brought into solution by treatment with aqua regia, and, after evaporating just to dryness on the water bath, the residue is treated with a little caustic soda, and then with sufficient sodium sulphide to bring it completely into solution—generally from 60 to 70 c.c. is sufficient. The antimony is deposited from this solution as described on p. 109.

The solution now contains arsenic and tin; it is acidified with dilute hydrochloric acid, whereby the arsenic and tin sulphides are precipitated. The mixed sulphides are filtered off and washed, and then washed through the filter paper, and digested with ammonium carbonate. The sulphide of arsenic passes into solution, and sulphide of tin is left behind; this is dissolved in ammonium sulphide, and the tin determined as described on p. 112.

The arsenic may be determined gravimetrically as sulphide, the solution in ammonium carbonate being acidified, a little sulphuretted hydrogen water being added to cause complete precipitation as sulphide; or the solution may be made up to a litre with distilled water, and from this litre 1 c.c. taken and diluted down again to 1 litre, and, if necessary, 1 c.c. again taken and diluted to 1 litre. Finally, 1 c.c. of this attenuated solution is placed in a Thorpe (p. 148) or Sand and Hackford (p. 150) arsenic apparatus, and the amount of arsenic determined by comparison with a standard arsenic mirror.

•Small quantities of copper, and occasionally bismuth, may be

present in Britannia metal. If a qualitative analysis shows these metals to be present, must be separated by the usual chemical methods.

### **Zinc Residues from Galvanising Bath.**

(Contained Zinc, Iron, Copper and Lead.)

A very hard alloy is obtained from the zinc residues left in the galvanising baths, the hardness and infusibility being due to the presence of iron in the zinc. In order to analyse such an alloy, it is dissolved in warm moderately dilute nitric acid. The solution is made up to the required volume, and about 10 c.c. concentrated nitric acid added. It is now electrolysed, using a large anode and a small cathode surface at a temperature of 60° or 70° and a C.D. of 1·5 amperes. In about two hours the whole of the lead will have been deposited on the anode as peroxide. Probably a portion of the copper—if there is any—will have been deposited upon the cathode, but on removing the anode, this immediately dissolves in the strong nitric acid. A fresh flag cathode is placed in the solution, which is then partially neutralised with ammonia and the copper deposited with a current of about 0·5 ampere. As soon as all the copper has been deposited, the solution is neutralised with ammonia; ammonium oxalate, and sufficient oxalic acid to make the solution just acid, added, and the zinc and iron deposited together.

The deposit, after weighing, is dissolved in dilute sulphuric acid, and the quantity of iron determined by titration with standard potassium permanganate. Or the iron and zinc can be determined separately by adding excess of ammonia, after the copper has been precipitated. The ferric hydrate thus precipitated is dissolved in oxalic or tartaric acid, neutralised with ammonia and determined as usual (see p. 100). The solution containing the zinc is neutralised with oxalic acid and deposited as described on p. 119.

The constitution, as would naturally be expected, of this alloy

varies considerably. The analysis of a sample was made in the above manner and checked by chemical means—

Zinc . . . . .	93.75
Iron . . . . .	3.65
Copper . . . . .	0.09
Lead . . . . .	1.53

The other constituents consisted of carbon and oxygen. Many samples examined contained no copper.

PART III  
PREPARATIONS BY ELECTROLYTIC  
MEANS



## CHAPTER XI.

### *PREPARATIONS.*

IN carrying out the preparations set out in the following chapters, it will often be necessary to separate the anode from the cathode by means of a porous membrane. The most usual form of diaphragm, or membrane, for this purpose is a cell of unglazed earthenware, such as is used in many forms of primary battery.

Before using these cells, they should be filled with water in order to ascertain whether they have actual holes through defects in manufacture. When filled with water, the outside of the cell should become moist within fifteen to thirty minutes, but the water should not actually trickle out. The porous cells can be obtained in a variety of forms; it is desirable to have them fairly thin in order that they may cause as little resistance to the passage of the current as possible. After having once been used, the cells should be kept in a basin and covered with cold water, otherwise they are very apt to disintegrate from the substances of the electrolyte crystallising in the pores.

One of the chief drawbacks to the employment of porous pots is, that as a rule they cannot be used for different experiments, owing to the difficulty of thoroughly cleaning them. For example, if a cell had been used in the preparation of iodoform, it could not satisfactorily be used afterwards in preparing—say azobenzene—because it would cause this second preparation to have the smell of the iodoform. Again, after a short time, especially in alkaline solution, the cells begin to disintegrate and break down, portions of the walls of the cell often falling off in flakes, or as a fine powder.

A form of cell illustrated in Fig. 53 gets over this difficulty. It is made either of Wedgwood ware or of a glazed material. The actual cell consists of two portions, one fitting within the other. Thus, in the figure, where two cells are shown, A fits into B, and C fits into D. Each complete cell consists of two perforated cells, the perforations being large enough for an ordinary pin to pass

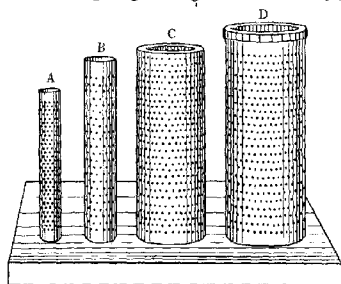


FIG. 53.

through, the inner or smaller of which fits loosely into the larger one. When put together, a liquid can pass readily through the complete cell, and of course it does not act as a diaphragm. In order to use the cell as a diaphragm, the inner cell is wrapped tightly with asbestos paper, until it can just be passed down into the outer cell. The asbestos should be wrapped in such a manner that there is considerable overlapping at the bottom end. This is then folded over so as to practically make a bag, and, when pushed home, the inner cell rests tightly upon the asbestos. Generally, about three folds of thin asbestos paper is sufficient to cause the one cell to fit tightly into the other. The cell prepared in this manner is soaked in water or the electrolyte, such, *e.g.*, as sulphuric acid or a salt solution, and is ready for use. When carefully packed, this makes a very efficient membrane, because since the two portions of the cell are, owing to the perforations, to all intents and purposes open to the passage of the current, the diaphragm employed, so far as resistance is concerned, is practically one of asbestos paper.

For most purposes, for sulphuric acid, which is not stronger than 25 to 30 per cent., or for moderate strengths of caustic alkali, and of course for neutral solutions, it is not necessary to employ asbestos, ordinary filter paper making an exceedingly effective diaphragm. As is well known, filter paper—blotting-paper—can be bought in sheets at a low cost, and the diaphragm is prepared by wrapping it several times round the inner cell in the manner described for asbestos. Parchment can also be employed, or a pulp of asbestos poured into the annular space between the two cells; a pulp of blotting paper has also been found to act very well, indeed ordinary brown paper has been used, and found quite satisfactory. Finally, coarse sand or coarsely powdered glass may be filled in between the pots, and makes an exceedingly good diaphragm, and will of course stand the action of the strongest acids and alkalis. It is sometimes a little difficult to obtain sand or powdered glass of quite the requisite degree of coarseness to prevent it passing through the holes, ordinary sand requiring first to be sifted through a sieve. Asbestos or a pulp of well-washed nitrated cotton wool can be very well used, even with strong acids and alkalis.

After the cells have been used, all that is necessary in order to clean them is to remove the inner cell from the outer one, throw away the substance which has been used as diaphragm, and the cells can then be readily cleaned, after which they are ready for further use.

It is sometimes found necessary in electrolysis to keep a small bag, containing the substance which is in solution and is being electrolysed, hanging in the solution in order to keep the concentration of the electrolyte constant. Now, a linen or muslin bag often gets acted upon, and more or less disintegrated by the electrolyte. One of the cells, above described, without a diaphragm will be found extremely useful for this purpose, because it allows free ingress and egress of the electrolyte. Of course, the substance used must not be so finely powdered that it passes through the perforations of the cell.



**Agitation of Solution.**—In the preparations to be described it will often be recommended to agitate the electrolyte. This can be done by means of paddles or fans, either of metal or of glass, wood or ebonite. Generally, it is an advantage to connect the stirrer with one of the poles of the circuit. Thus, when oxidising an organic substance, a stirrer of platinum or lead can be satisfactorily employed, and is connected with the positive pole. Fig. 54 shows such a stirrer made of platinum; the method of making contact has already been described on p. 81, Fig. 48.

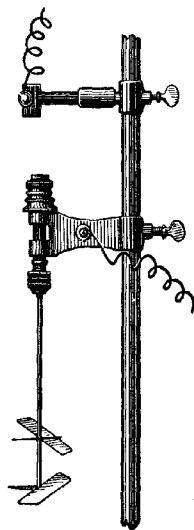


FIG. 54.

The lead stirrer may be made as follows:—Thin lead pipe, to which the vanes for mixing the liquid are “burned” or soldered, is drawn over a steel rod of the same diameter as the bore of the pipe. The steel rod protrudes about 5 to 10 cm. above the top of the pipe, in order that it may be fastened in the chuck. The pipe is burned or soldered at the bottom and top to prevent the solution from running in between it and the

steel core. If a central core of steel is not used, lead electrodes are not sufficiently rigid to be used for rotating purposes. For diagram of glass stirrer, see p. 272.

**Electrodes.**—The electrodes employed in this section of the book are usually of platinum, lead, nickel or graphite. The platinum is used as wire, foil, or gauze; platinum is joined to platinum almost invariably by welding, which is an easy process to carry out. Suppose, for example, it is desired to weld a piece of wire to a sheet of platinum. The sheet platinum is laid upon a flat piece of smooth iron or steel, *e.g.* an anvil, the wire is

held against the sheet with a pair of pliers, and the flame of a blowpipe caused to play upon the sheet and wire. When the platinum has reached a bright red heat, the wire is struck a sharp blow with a hammer, the flame of the blowpipe is kept on the point to be hammered, and the hammering continued until a good welded joint has been produced.

Every electro-chemist should be able to make his own electrodes, and must therefore be able to use a soldering iron. The form or shape of an electrode employed will be modified by circumstances and by the ingenuity of the operator. The best form of graphite to use for carbon electrodes is the "Acheson" artificial graphite, made at the Niagara Falls. It is an excellent conductor, and has the enormous advantage over other forms of carbon electrodes, that it can be easily cut and machined.

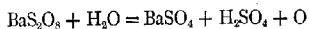
## CHAPTER XII.

### *PREPARATION OF INORGANIC PRODUCTS.*

#### **Persulphuric Acid.**



ONE of the first substances to be prepared by electrolytic methods, and which had not previously been obtained by purely chemical means, was persulphuric acid. Sulphur heptoxide  $\text{S}_2\text{O}_7$ , the anhydride of persulphuric acid, was discovered in 1878 by Berthelot, who obtained it by the action of the silent electric discharge on a well-cooled mixture of oxygen and sulphur dioxide. He also showed that when a moderately concentrated solution of sulphuric acid is electrolysed, the acid in the neighbourhood of the anode, after the passage of the current, possesses oxidising properties. Further, that on addition of barium chloride to the sulphuric acid solution, and filtering off the precipitate of barium sulphate, and then boiling the filtrate, another quantity of barium sulphate was produced, the soluble barium salt of persulphuric acid having been decomposed on boiling into barium sulphate, sulphuric acid, and oxygen.

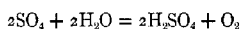


#### **I. Preparation of Persulphuric Acid.**

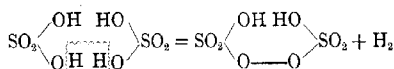
Persulphuric acid can be produced both with and without a diaphragm. In the latter case, when the electrolysis is conducted in such a manner that the anode is placed considerably below

the cathode, practically no intermingling of the upper and lower layers of sulphuric acid takes place, and persulphuric acid is formed round the anode.

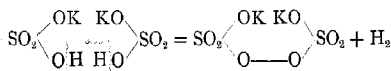
Dilute sulphuric acid is supposed to contain the ions  $2\text{H}^+$  and  $\text{SO}_4^{--}$ , and, on electrolysis, hydrogen is yielded up at the cathode, and the  $\text{SO}_4^{--}$  has its electrical charge neutralised at the anode; but since  $\text{SO}_4$  is incapable of existence in the molecular condition, it reacts with a molecule of water, and oxygen gas is given up at the anode.



But when a fairly concentrated solution of sulphuric acid (50 to 60 per cent.) is electrolysed and the solution kept cool, it is noticed that, although hydrogen is given off as vigorously as usual at the cathode, very little oxygen is evolved at the anode. In strong sulphuric acid we assume that the ions, instead of being  $2\text{H}^+$  and  $\text{SO}_4^{--}$ , are mainly  $\text{H}^+$  and  $\text{HSO}_4^{'}$ . Now, on electrolysing such a solution, hydrogen is yielded up at the cathode; but at the anode the ions  $\text{HSO}_4^{'}$ , at the moment of having their electrical charge neutralised, unite together to produce a molecule of persulphuric acid thus:—



Similarly, a strong solution of an acid sulphate, *e.g.* potassium hydrogen sulphate, is ionised into the ions  $\text{H}^+$  and  $\text{KSO}_4^{'}$ , and on electrolysis a persulphate is produced.



The conditions necessary are a high anode current density and a cold solution; the temperature of the solution should not be allowed to rise above  $+5^\circ$ .

A very convenient apparatus for demonstrating the formation of persulphuric acid and persulphates is shown in Fig. 55.

A is a large boiling tube which is nearly filled with a solution

of 50 to 60 per cent. sulphuric acid, or a saturated solution of acid potassium sulphate. The tube B, which is open at both ends, is supported in A by means of a piece of copper wire or by a

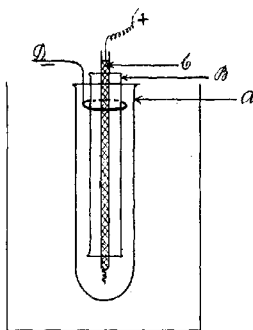


FIG. 55.

perforated cork, notched at the edges to allow the escape of gases. C is a narrow glass tube, at the lower end of which a small spiral of platinum wire is fused. It is filled with mercury, and connected with the + pole of the current supply. D is the cathode of stout platinum wire. The whole apparatus is placed in a beaker filled with cold water. On passing the current, about 1 ampere, hydrogen is evolved at the cathode, and, as this is

close to the surface of the solution, the hydrogen passes into the air without mixing with the solution round the anode. Any oxygen which is given off at the anode passes up the tube B. After the current has been passing for a short time, a small portion of the solution may be withdrawn from the neighbourhood of the anode by means of a pipette. On adding a solution of potassium iodide to it, iodine is liberated, thus showing the presence of persulphuric acid. The conditions necessary are a high current density at the anode, and a cold solution. Although the actual current registered on the ammeter is only about 1 ampere, yet, owing to the very small surface of the anode, the current density will be from 60 to 80 or more amperes per square decimeter.

For studying the course of the reaction, by titration with ferrous ammonium sulphate (see p. 205), it is better to employ the apparatus depicted in Fig. 56. The solution should be well mixed, and then 10 c.c. withdrawn by means of a pipette, and the solution titrated, the operation being repeated every 45 minutes, and continued until the maximum amount of persulphuric acid is obtained: the current efficiency may then be calculated.

When potassium hydrogen sulphate is electrolysed under the same conditions, after the current has been passing for some ten or twenty minutes, a cloud of potassium persulphate begins to separate round the anode. In making the solution of acid potassium sulphate, a saturated solution should be made at normal temperature, and then cooled down before being placed in the apparatus, otherwise crystals of acid potassium sulphate may separate out during the electrolysis, and will interfere with the reaction.

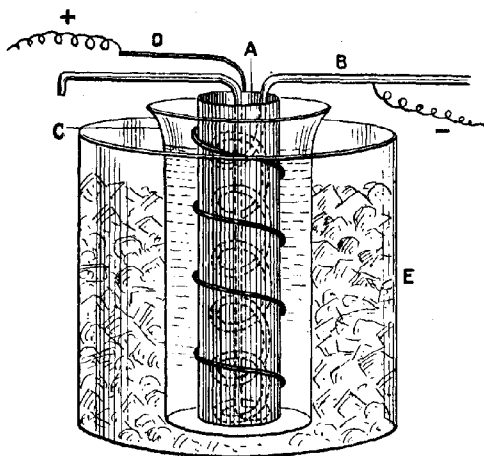


FIG. 56.

## II. Preparation of Potassium Persulphate, using a Diaphragm.

A porous pot, A (Fig. 56), is made the cathode compartment, the cathode being a coil of lead or copper tube, B, through which cold water is circulated, so that the solution may be kept quite cool. In order to make electrical connection, a piece of copper wire is soldered on to the coiled pipe, and connected with

the negative pole of the current supply. The cathode solution consists of 50-per-cent. sulphuric acid.

The anode is a coil of thin platinum wire, D, wound about three times round the outside of the cathode compartment; it should be of such a surface that, with a registered current of 5 or 6 amperes, a current density of 50 or 60 amperes is obtained. The porous pot and the anode are then placed into a beaker, C, of about 600 to 700 c.c. capacity, the whole apparatus being placed in a glass basin, and surrounded with ice or a mixture of ice and salt. The anode solution is a saturated solution of acid potassium sulphate, containing a few cubic centimeters of dilute sulphuric acid. For most experiments, when only small quantities of the persulphate are required, a porous cell with a capacity of 100 to 120 c.c. may be used. This is placed in a beaker or glass jar of such capacity that only about 200 to 250 c.c. of the saturated solution of potassium bisulphate is required to practically fill it.

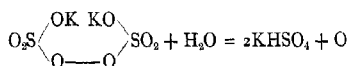
As the electrolysis proceeds, and the potassium persulphate separates out, the concentration of the acid potassium sulphate decreases. In order to keep the solution constantly saturated, a small perforated cylinder, such as is described on p. 196, Fig. 53, filled with crystals of potassium hydrogen sulphate, is supported in the upper portion of the anode compartment, where it is held in position by means of a clamp.

Müller finds that the yield of persulphates is increased by the addition of small quantities of hydrofluoric acid. When this acid is added, the electrolysis must be conducted without a diaphragm, and the glass vessel must be coated with paraffin to prevent the HF acting upon the glass; probably a celluloid vessel could be satisfactorily employed.

### III. Ammonium Persulphate.

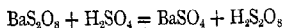
The same apparatus and conditions as are employed for the preparation of potassium persulphate are used for preparing the ammonium salt. The anode solution consists of a concentrated solution of ammonium sulphate in a solution of 5-per-cent. sulphuric

acid. The preparation of ammonium persulphate is more satisfactory than that of the potassium salt, because the acid ammonium sulphate is more soluble in water. The perforated cylinder for keeping the concentration constant is in this case filled with crystals of ammonium sulphate. Persulphuric acid and the persulphates are derivatives of hydrogen peroxide, as is shown by the structural formula. When a solution of persulphuric acid or a persulphate is heated, oxygen gas is evolved.

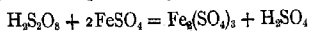


The persulphates are therefore very powerful oxidising agents: the action is not very rapid, but it is very thorough; this is probably due to the fact that they are fairly stable, and are not rapidly decomposed. A mixture of a persulphate and sulphuric acid is known as Caros acid, and is often employed in organic chemistry, owing to its extremely powerful oxidising action.

The barium salt of persulphuric acid is soluble in water; we have therefore here a means of separating this acid from sulphuric acid. In order to do this, excess of barium hydrate is added to the mixed solution, when barium sulphate is precipitated, and may be filtered off. The solution now contains a mixture of barium hydrate and barium persulphate; by careful addition of sulphuric acid, until no further precipitate is produced, a solution containing persulphuric acid is obtained.



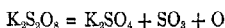
**Estimation of Persulphuric Acid.**—The quantity of persulphuric acid in a solution can be estimated by means of ferrous ammonium sulphate, which is oxidised to the ferric condition. The operation may be carried out by adding an excess of a solution of ferrous ammonium sulphate of known strength and titrating back with potassium permanganate.



In carrying out the operation, a known volume of the acid solution, or a weighed quantity of a persulphate (dissolved in



water) is taken, and a considerable excess of a solution of ferrous ammonium sulphate, of known strength, added, and also dilute sulphuric, about 5 c.c. to every 10 c.c. of solution; then about 100 c.c. of boiling water is poured into the mixture, which is immediately titrated back with potassium permanganate.<sup>1</sup> If the hot water is not added, the reaction between the ferrous salt and the persulphate is slow, only being completed after some considerable time. It is not necessary to add sulphuric acid when a solution containing persulphuric acid and sulphuric acid is to be titrated. Potassium or sodium persulphate can be determined by simply heating a weighed portion of the salt.



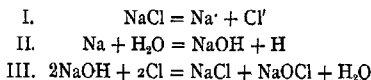
The loss in weight shows the amount of persulphate which was present in the sample taken.

#### LITERATURE.

Berthelot, *Compt. Rendus*, **86**, 20, 277; H. Marshall, *Journ. Chem. Soc.*, **1891**, 771; Berthelot, *Comp. Rendus*, **114**, 876; K. Elbs and O. Schönherr, *Zeit. f. Elektrochem.*, 1894, I. 417; K. Elbs, *Journ. f. prakt. Chem.*, 1893, **48**, 158; *Zeit. Elektrochem.*, 1895, **2**, 245; A. R. Foster and E. F. Smith, *Amer. Chem. Soc.*, 1899, **21**, 934; H. Marshall, *Chem. News*, **83**, 76; Le Blanc and Eckardt, *Zeit. f. Elektrochem.*, V. 355; Müller, *Zeit. f. Elektrochem.*, X. 776 (1904).

### IV. Sodium Hypochlorite.

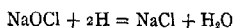
When a strong solution of sodium chloride is electrolysed in the cold, without a diaphragm, the main product produced is sodium hypochlorite. The reaction in its simplest form may be represented by the following equations:—



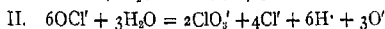
It would therefore appear that, if the electrolysis is continued for a sufficiently long time, a large proportion of the chloride will

<sup>1</sup> Le Blanc and Eckardt, *Zeit. f. Elektrochem.*, V. 355.

become converted to hypochlorite. This, however, for several reasons, is not the case. In the first place the hydrogen, at the moment of its liberation at the cathode, exerts a reducing action upon the hypochlorite, regenerating sodium chloride.



In order to obtain the minimum of reduction, the cathode should be smaller than the anode; that is to say, a high current density at the cathode should be employed. Under these conditions the reducing action of the hydrogen is localised, and there is more chance for the hydrogen atoms to unite to form molecules without first acting upon the hypochlorite. On the other hand, the C.D. at the anode need not be quite so high as that at the cathode, but neither must it be very low. When the current density is low, very little oxygen is given off at the anode; this, of course, prevents oxidation of the hypochlorite to chlorate, but the amount of hypochlorite produced is not so great, because, after a certain quantity of hypochlorite has been produced there are present  $\text{Na}^+$  and  $\text{OCl}^-$  ions. The  $\text{OCl}^-$  ions help to carry the current, and, being discharged at the anode, cause oxygen to be liberated and hypochlorous and chloric acids to be formed.



Now, since the  $\text{OCl}^-$  anions are relatively more readily discharged at the anode than the  $\text{Cl}^-$  ions, *i.e.* less energy is required for their discharge, the tendency is for a considerable amount of the electrical energy to be wasted in these secondary changes. To prevent this as far as possible, a high anode C.D. and good circulation of the electrolyte are desirable, but in order to prevent cathodic reduction, the cathode is kept smaller than the anode. For example, with an anode of one square decimeter the cathode might have an area of 0.75 sq. dm.

But there are also other methods for preventing cathodic reduction. It is found that if the sodium chloride used contains a small quantity of a calcium salt, that a thin pellicle of calcium

hydrate is produced on the cathode. This pellicle scales off, but is immediately reformed. Now, since there is a high current density at the anode, anything which will momentarily hinder the gas on its liberation from coming in contact with the electrolyte will tend to cause union of the atoms to molecular hydrogen. When the hydrogen has once assumed the form of molecules, then its reducing power is at an end. This very unstable membrane or diaphragm of calcium hydroxide is able to cause the union of the atoms to a very large extent. Foerster has found that a small quantity of an alkali chromate gives even better results than a calcium salt. The quantity of chromate required is extremely small (0.5 to 1 per cent.), and yet it is remarkably effective. The temperature should not be allowed to rise above 20°, because the higher the temperature the greater the inclination to form chlorates.

**Process.**—A glass battery-jar of about 500 to 700 c.c. capacity is nearly filled with a saturated solution of common salt. If the solution is not clear, it should first of all be filtered. It is best to use both anode and cathode of platinum, but the cathode may be of nickel or graphite, and graphite can also be substituted for the platinum anode. The cathode should be in the form of a spiral of stout wire, in order that as high a C.D. as possible may be employed. The anode may either be of sheet platinum or of platinum wire, but the most satisfactory results, on a small scale, are obtained when a rotating anode is used, such, *e.g.*, as that described on p. 198.

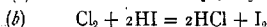
#### CONDITIONS.

Anode C.D. . . . .	12 to 16 amperes.
Cathode C.D. . . . .	20 to 30 amperes.
E.M.F. . . . .	3.5 to 4.5 volts.
Temp. . . . .	18° to 20°

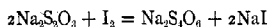
If the anode is not rotated, it should be fixed at the opposite side of the electrolysing vessel to the cathode, and should be kept near the upper portion of the solution. Agitation of some form or other is to be recommended. As the C.D. employed is very high, the platinum wire carrying the current should be stout in

order to prevent heating. To carry this current without undue heating, the wire should be from 1.5 to 2 mm. in diameter.

In order to study the course of the electrolysis, 10 c.c. of the solution is withdrawn every half-hour, and titrated. To this quantity of solution is added excess of a solution of potassium iodide, and the mixture is then acidified with dilute hydrochloric acid.



The amount of the liberated iodine is then determined by means of  $\frac{\text{N}}{10}$  thiosulphate, in the usual way.



It is very instructive to follow the course of the electrolysis by analysing the gases evolved at stated intervals. To do this, a gas coulometer should be placed in series with the hypochlorite cell. The electrolysing cell must be closed with a rubber stopper through which a delivery tube passes. The amount of current which is being passed in during, say, ten minutes is easily measured by the coulometer, and this can be compared with the quantity of gas which escapes from the electrolysing cell. The gases will consist of oxygen and hydrogen, with a trace of chlorine; this latter can, however, be neglected. The gases are collected in a Hempel's burette, and the quantity of oxygen estimated by absorption with alkaline pyrogallol. The loss of hydrogen shows the quantity of the gas which is being used up in reducing the hypochlorite.

Titration and gas analytical experiments should be tried with plain sodium chloride solutions, and with solutions containing a small quantity of potassium chromate. Curves showing the current efficiency and yield of hypochlorite in a given time should then be plotted.

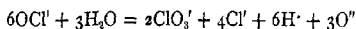
#### LITERATURE.

F. Oettel, *Zeit. Elektrochem.*, 1894, 1, 69 and 356; *Chem. Zeitung*, 1894, 18, 69; H. Bischoff and F. Foerster, *Zeit.f. Elektrochem.*, 1897, 4, 464; A. Sieverts, *Elektrochem.*, 1899, 6, 364 and 374; F. Oettel, *Zeit.f.*

*Elektrochem.*, 1900, **7**, 315 and 449; Viktor Engelhardt, *Zeit. f. Elektrochem.*, 1900, **7**, 390, and Viktor Engelhardt, *Hypochlorite u. Elektrische Bleiche* (Wilhelm Knapp, 1903).

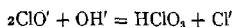
## CHLORATES.

In the second equation, on p. 207, it has already been shown that when hypochlorite anions take part in the electrolysis, they are on discharge converted into chloric ions.

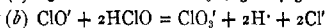
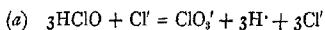


Now, the conditions of electrolysis of chlorides can be so altered that the final product will be a chlorate. But the reaction just referred to is not the only one which occurs when chlorates are produced.

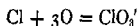
In all probability the production of hypochlorites is always the first stage in the reaction, and that then, partially through the hypochlorite taking part in the electrolytic process and being oxidised at the anode, we may get:



This primary oxidation probably takes place in a slightly alkaline solution in which there are free OH ions. But in an acid solution (solution containing a bicarbonate) we probably get—



In an alkaline solution direct oxidation of the chlorine ions may also take place.

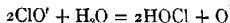


The equations just given may all take place in the cold, but in order to obtain the best results in the preparation of chlorates, a hot solution is always employed, and therefore the following equation also takes place, and is probably the main reaction:—



When the electrolysis is conducted at high temperatures, perchlorate is not produced, but it is formed in cold solutions. In the

electrolytic preparation of chlorates, a certain quantity of oxygen is invariably given off, which is probably due to the hypochlorite ions taking part in conveying the current.



In preparing hypochlorites it has already been found that the reducing action of the hydrogen can, to a very large extent, be prevented by the addition of small quantities of calcium salts or of chromates. In preparing chlorates, the addition of a small quantity of potassium chromate is even more advantageous.

In the preparation of chlorates the following points are of importance:<sup>1</sup>—

I. Prevention of cathodic reduction, *e.g.* by addition of calcium salts or potassium chromate.

II. Slight acidity of the solution in order to aid the formation of free hypochlorous acid. This can be brought about by passing a stream of carbonic acid gas through the solution.

III. The employment of sufficient volume of solution in proportion to the C.D., and good agitation of the electrolyte, to allow the secondary reactions to take place as completely as possible.

IV. The temperature to be at least 40° in order to prevent the formation of perchlorates, and also to lower the resistance and therefore the E.M.F.

## V. Preparation of Potassium Chlorate.

Make a saturated solution of potassium chloride at 40° or 50°, and to every 100 grm. of potassium chloride add 1 grm. of potassium carbonate and 1 grm. of potassium dichromate. The solution is then poured into a beaker of about 400 c.c. capacity, which is placed on a sand bath, so that the temperature can readily be maintained at from 45° to 60°. The anode must be platinum; the rotating anode is the most satisfactory to employ, but a piece of sheet platinum, or, better, platinum gauze, may be used. The

<sup>1</sup> *Jahrbuch*, 1899, VI. 207.

cathode should also be of platinum—preferably stout wire—but a graphite rod or a spiral of thick nickel wire may be employed.

#### CONDITIONS.

C.D. . . . .	18 to 20 amperes at anode.
E.M.F. . . . .	4·7 to 5·7 volts.
Temp. . . . .	45° to 60°

A slow stream of carbonic acid gas is also conducted through the electrolyte; this is in order to convert the potassium carbonate into potassium bicarbonate. If a platinum stirrer is not at hand to use as anode, it is advisable to agitate the solution with a stirrer of glass. When preparing sodium hypochlorite, it will be remembered that the electrodes were placed a considerable distance from each other. In the preparation of chlorates, however, they should not be more than 1 cm. apart.

After the current has passed for some time, crystals of potassium chlorate sometimes commence to fall out, and, on cooling, after allowing the current to pass for some three hours, large quantities of the salt crystallise out. These crystals, after filtering and washing with cold water, will be found to be almost free from chloride, and after one crystallisation they are obtained quite pure. By evaporating down the mother liquor, a further quantity of crystals is obtained, but they are not quite so pure as the first crop.

If it is desired to obtain a large quantity of potassium chlorate, a perforated cell (Fig. 53, p. 196) filled with potassium chloride may be suspended in the electrolyte; by this means the solution will be always saturated with potassium chloride, and the process made continuous. The current yield is fairly good, generally being between 65 and 70 per cent.

**Sodium Chlorate** can be prepared in the same manner; but, owing to the relative solubility of sodium chlorate to sodium chloride, it is not so easy to obtain a complete separation of the two substances.

## VI. Potassium Bromate.

Dissolve 70 gm. of potassium bromide in 200 c.c. of water, and add 0·5 gm. potassium dichromate. The electrodes used

for potassium chlorate can be employed for the electrolysis of bromide solutions. The temperature of the bath should be kept at about  $40^{\circ}$ , otherwise the conditions are practically the same as those employed in the preparation of chlorates.

## CONDITIONS.

C.D. . . . .	11 to 12 amperes at anode.
E.M.F. . . . .	4.3 to 5.0 volts.
Temp. . . . .	$38^{\circ}$ to $40^{\circ}$

As a rule, the potassium bromate does not commence to crystallise out until the solution is cooled. The quantities given above require the passage of about 75 ampere hours of current.

**Sodium Bromate** can be prepared in a similar manner; but it is even more difficult to separate from sodium bromide, than sodium chlorate from sodium chloride.

The theoretical considerations given for the electrolytic production of chlorates apply also to the preparation of bromates. But it is found that bromates are much more readily reduced in an alkaline solution than are chlorates.

## VII. Potassium Iodate.

Dissolve 50 gm. potassium iodide in 200 c.c. water, add 1 gm. potassium carbonate and 0.5 gm. potassium dichromate.

## CONDITIONS.

C.D. . . . .	11 to 12 amperes at anode.
E.M.F. . . . .	4.3 to 5.2 volts.
Temp. . . . .	$40^{\circ}$

After passing about fifty ampere hours of current, the electrolysis is stopped, the solution evaporated to about half its bulk, and allowed to stand overnight in a cool place to crystallise. The current efficiency is very good.

## LITERATURE.

There is a great deal of literature upon the electrolysis of chlorides, and the preparation of chlorates, etc. The easiest way to study the subject is to read the *résumé* in the *Jahrbuch* for 1898, p. 186; and 1899, p. 198; also 1902, p. 357.



### VIII. Potassium Perchlorate.

Chlorates can be further oxidised by the electric current to perchlorates. In fact, both chlorates and perchlorates, especially the former, are manufactured on a large scale by the electrolysis of chlorides. Indeed, nearly all the chlorates at present manufactured are made by the electrolytic process.

**Method.**—Prepare a cold saturated solution of potassium chlorate, and, in order that the solution may remain saturated, a perforated cell filled with potassium chlorate is suspended in the solution.

Electrodes of sheet platinum or platinum gauze should be used, and the electrolyte must not be agitated—at any rate, not continuously agitated—although an occasional stir is an advantage. The electrolyte must not be allowed to become alkaline; in order to prevent this, it is better to add a few drops of dilute sulphuric acid to make the solution just acid—the acidity may, however, only be very slight.

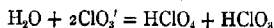
#### CONDITIONS.

C.D. . . . .	9 to 12 amperes at the anode.
E.M.F. . . . .	8·5 to 16 volts.
Temp. . . . .	Not above 20° or 24°

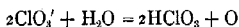
As the current density employed is fairly high, there is a tendency for the electrolyte to become heated. It is therefore best to stand the electrolytic cell in a basin of cold water, which is continually filled by water running in, and at the same time siphoning out.

When the current has passed for from thirty to forty minutes, the potassium perchlorate begins to rain down from the neighbourhood of the anode in the form of brilliant crystal plates. If the C.D. rises too high, it is rather difficult to keep the solution sufficiently cool.

When the solution is kept cold, and is not alkaline, the reaction which takes place may be represented by the following equation :—



The appearance of any quantity of oxygen gas at the anode points to the reaction going mostly in the following manner:—



There is always a small quantity of oxygen given off at the anode; but it will be noticed that this increases very rapidly if the temperature is allowed to rise much over 20°.

**Potassium perbromate** is readily prepared in the same manner as the perchlorate, but the preparation of the periodate is attended with considerable difficulties, and it is necessary to keep the solution alkaline. Müller and Friedberger have succeeded in obtaining the free periodic acid by electrolysing iodic acid in the anode compartment.

#### LITERATURE.

Foerster, *Zeit. f. Elektrochem.*, **4**, 386; Winteler, *Zeit. f. Elektrochem.*, **5**, 49, and 217; Müller, *Zeit. f. Elektrochem.*, **7**, 509; Müller and Friedberger, *Ber.*, **35** (3), 2652.

### IX. Lead Peroxide.

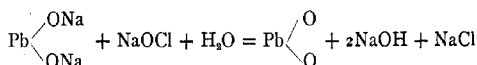
Litharge (lead monoxide) can be electrolytically oxidised to its higher oxide lead peroxide. The operation is carried out by electrolysing a solution of sodium or other alkali chloride in which litharge is suspended.

**Process.**—Twenty grm. of litharge is suspended in a 20-per-cent. solution of sodium chloride, contained in a battery jar of about 500 to 700 c.c. capacity. The cathode is hung at one side of the jar, the anode at the other; the cathode may be of lead or graphite, but it should be wrapped in a piece of parchment, or surrounded with a piece of asbestos paper, and placed in one of the smaller perforated cells described on p. 196, Fig. 53. The anode can be either of platinum or graphite. The mixture must be very vigorously agitated, either by rotating the anode, or by having a separate arrangement for agitating the mixture.

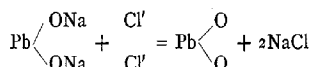
#### CONDITIONS.

C.D. . . . .	1 to 1·5 ampere.
E.M.F. . . . .	3·5 to 4 volts.
Temp. . . . .	Normal.

As the electrolysis proceeds, the oxide gradually becomes light brown, and, finally, dark brown, showing that all the PbO has been changed to PbO<sub>2</sub>. At the end of the reaction, the lead peroxide is filtered off, washed with water to free it from adhering chloride, and warmed with moderately dilute nitric acid, in order to dissolve out any unchanged lead monoxide. During the electrolysis no chlorine will be liberated, because sodium hypochlorite is produced. The formation of the lead peroxide is, indeed, due to the action of the hypochlorite upon the lead monoxide, a small portion of which becomes dissolved as sodium plumbite.



And also to a certain extent to the direct action of chlorine ions on the sodium plumbite.



It is important that the litharge should be well ground, otherwise it is inclined to be only superficially oxidised. This process is of commercial importance, lead peroxide among other uses being largely employed in the match industry.

#### LITERATURE.

Elbs and Forssell, *Zeit. f. Elektrochem.*, **8**, 760, D.R.P., 1900, 124512.

### X. White Lead.

There are several electrolytic methods for preparing white lead; most of them, however, are indirect. The method of Luckow is direct, the lead necessary for the production of the white lead being obtained from a lead anode, which goes into solution as the current is passed. The chief drawback is the extremely dilute solutions which are employed. The manufacture

of white lead by this process was carried on for some time at Cologne.

**Process.**—12 grm. of sodium or potassium chlorate and 3 grm. of sodium carbonate are dissolved in 1 litre of water. Both the anode and cathode consist of sheet lead, which is hung about 2 cm. from the bottom of the electrolysing cell.

## CONDITIONS.

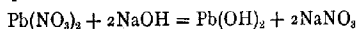
C.D. . . . .	0.4 to 0.6 ampere.
E.M.F. . . . .	1.8 to 2 volts, electrodes 1 cm. apart.
Temp. . . . .	Normal.

During the electrolysis a slow stream of carbonic acid gas is passed into the solution, behind the cathode; it should be passed in such a manner that the fluid is as little disturbed as possible, so that the white lead produced may sink to the bottom of the cell.

Almost as soon as the electrolysis commences, a thin white pellicle forms on the anode, which continually peels off during the time the current is passing. The electrode at the end of the reaction has a bright metallic appearance, as if it had been freshly cleaned.

The sodium chlorate causes the lead anode to go into solution as lead chlorate; this is then acted upon by the sodium carbonate, which with the water forms hydrated lead carbonate. The carbonic acid is passed into the solution to prevent formation of sodium hydrate; at the same time, it should not be passed in sufficiently rapidly to produce sodium bicarbonate.

An extremely interesting indirect process is that patented by Browne and Chaplin. In this process a solution of sodium nitrate is electrolysed in a divided cell, with a lead anode and a copper cathode. In the cathode compartment sodium hydrate is produced, in the anode cell nitric acid; this causes the lead anode to dissolve with formation of lead nitrate. After the electrolysis is finished, the solutions are mixed, when lead hydrate and sodium nitrate are produced.



The lead hydrate is then converted into white lead by addition

of sodium carbonate; and the regenerated sodium nitrate can then be again employed for production of a further quantity of lead nitrate and caustic soda.

## XI. Chrome Yellow.

Luckow's method for preparing white lead can also be employed for producing other mineral colouring matters, such, *e.g.*, as chrome yellow; in this case, sodium or potassium chromate is employed instead of sodium carbonate. The current conditions are the same as in the preparations of white lead. At the commencement of the electrolysis the chrome yellow which falls off from the anode has a fine fiery appearance. But after a short time it becomes reddish and smeary looking, consequently it is not possible to obtain good quality chrome yellow in quantity by this method.

### LITERATURE.

Borschers, *Zeit. f. Elektrochem.*, **3**, 482; Luckow, *D.R.P.*, 91707 and 105143; Browne and Chaplin, *U.S.P.*, **1895**, 551361, and **1896**, 555,232; Le Blanc and Bindschedler, *Zeit. f. Elektrochem.*, **8**, 255; A. Isenburg, **9**, 275.

## XII. Potassium Permanganate.

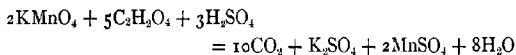
Prepare a strong solution of potassium carbonate, about 40 per cent, such a solution has a sp. gr. of about 1.42. The object of employing a solution as strong as this is that the permanganate is much less soluble in a concentrated solution of potassium carbonate than in weaker solutions. This solution of potassium carbonate can be used both for anode and cathode.

The anode consists of a piece of ferromanganese or of metallic manganese. Ferro-manganese can be obtained with a very high percentage of manganese, but pure manganese, absolutely free from iron, is not so readily obtained. The presence of iron in the ferro-manganese does not, however, exert any harmful effect, the iron being simply precipitated as hydrated carbonate.

The ferro-manganese is, when not obtainable in rods, wound round with platinum or iron wire, which is connected with the positive pole of the current supply. The cathode of iron or other metal is placed in a porous cell, which stands in a beaker containing the potassium carbonate. The best form of porous cell to use, when the solution is so strongly alkaline, is the perforated cell described on p. 196, with a diaphragm of asbestos, or better sand.

As soon as the current—the strength of which may vary within wide limits—is passed, permanganate begins to form, and flows off the anode in purple streams; in a short time the whole anode solution becomes deep purple.

The course of the electrolysis, and the current efficiency, can be followed by titrating with oxalic acid.

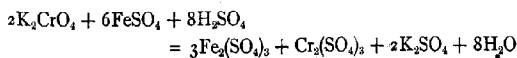


It is possible to prepare potassium permanganate without separating the anode from the cathode. In this case the cathode is made of the positive plate of an accumulator or of the copper oxide plate of a cupron cell.

Any ferric hydrate which is produced during the reaction is precipitated to the bottom of the anode cell. When the current is passed for a sufficient length of time, crystals of potassium permanganate separate out.

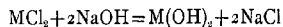
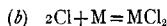
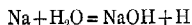
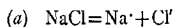
### XIII. Potassium Chromate.

If instead of using an anode of ferro-manganese, one of ferro-chrome is employed in a solution of potassium hydrate, then a solution of potassium chromate is produced. As is the case in the preparation of potassium permanganate, ferric hydrate is produced from the iron in the ferro-chrome; this is, of course, precipitated, and can be filtered off. The course of the electrolysis should be followed by titration from time to time with ferrous ammonium sulphate.



#### XIV. Metallic Hydroxides.<sup>1</sup>

When a metal is made the anode in a solution of an alkali chloride, nitrate or sulphate with an insoluble cathode such as graphite or platinum or a strip of the same metal employed as anode, the metal at the anode is dissolved, and a metallic hydroxide produced. The formation of the hydroxide is due to the metallic salt produced at the anode coming into contact with the alkali hydroxide liberated at the cathode.



(M is a divalent metal.)

Since, when a metal is made the anode and goes into solution, partial disintegration invariably takes place, and particles of the metal fall to the bottom of the electrolysing cell, thus contaminating the electrolyte, the anode should be wrapped in a piece of cloth or, better, parchment, to prevent this happening.

In the preparation of these hydroxides, it is advantageous to keep the solution well agitated. One of the easiest ways of doing this is to cause the anode or the cathode to rotate. This is readily done by soldering a piece of stout wire to the electrode, and fixing it in the chuck of the rotating arrangement described on p. 80.

One great advantage in this method of preparing hydroxides is, that the solution always remains neutral. For this reason there is no possibility of dissolving hydroxides which have an acidic character; further, the amount of alkali salt in the solution never increases beyond the quantity which was originally present, and thus washing of the precipitate is easy.

The material of the electrolyte exerts considerable influence upon the nature of the hydroxide produced; thus in 10-per-cent.

<sup>1</sup> Lorenz, *Zeit. f. Anorg. Chem.*, **12**, 396 and 436.

solutions of sodium chloride, potassium nitrate and sodium sulphate, the following compounds are formed, with various anodes.

	Sodium chloride.	Potassium nitrate.	Sodium sulphate.
Cadmium . . . . .	$\text{Cd(OH)}_2$	$\text{Cd(OH)}_2$	$\text{Cd(OH)}_2$
Copper . . . . .	$\text{Cu.OH}$	$\text{Cu(OH)}_2$	$\text{Cu(OH)}_2$
" . . . . .	$\text{Cu}_2\text{O}$ at $100^\circ$	$\text{CuO}$ at $100^\circ$	$\text{CuO}$ at $100^\circ$
Lead . . . . .	—	$\text{PbO}_2$	—
Iron . . . . .	$\text{FeO}$	$\text{Fe}_2\text{O}_3$	$\text{FeO}$
Mercury . . . . .	—	$\text{Hg}_2\text{O}$	—
Tin . . . . .	$\text{Sn(OH)}_2$	$\text{Sn(OH)}_2$	$\text{Sn(OH)}_2$

Except in the case of copper, where the anhydride of the oxide is produced at high temperatures, it is better to work at a temperature of from  $70^\circ$  to  $80^\circ$  or higher, because, when the hydroxide is formed at high temperatures, it is more readily filtered and washed.

## XV. Metallic Sulphides.

### Cadmium Sulphide (Cadmium Yellow).

Metallic sulphides can be obtained in an analogous manner to that in which metallic hydroxides are prepared. Copper sulphide is made the cathode in a solution of an alkali chloride, nitrate, or sulphate, and the metal the sulphide of which it is desired to prepare the anode. Copper sulphide is practically the only sulphide which can be employed as cathode because it conducts the current readily, whereas most sulphides do not conduct the current at all, or conduct it very poorly. When the copper sulphide can be obtained in the form of a rod, there is no difficulty in forming the cathode; it must, however, be wrapped in cloth or parchment to prevent particles falling to the bottom and contaminating the product. Generally copper sulphide is obtained in the form of a coarse powder; when in this form, the only way to make the cathode is to pack the sulphide closely round a piece of copper wire in a porous pot or in a stout linen bag. It should then be electrolysed for a short time with an



insoluble anode, that the outer portions of the cell may become saturated with the alkali sulphide.

In order now to prepare cadmium sulphide, an anode made from a rod of cadmium is placed in the bath, containing a 10-per-cent. solution of sodium chloride, nitrate, or sulphate. The anode should be wrapped round with a piece of calico to prevent disintegrated portions falling into the electrolyte. The solution must also be agitated, and the simplest method is to cause the anode to rotate (see p. 220).

#### CONDITIONS.

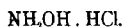
C.D. . . . .	1 to 2 amperes.
E.M.F. . . . .	3 to 4 volts.
Temp. . . . .	60° to 70°

Almost as soon as the circuit is closed, a yellow precipitate of cadmium sulphide commences to fall down. Generally a small amount of cadmium hydroxide contaminates the sulphide, owing to the cathode reaction being a little slow; therefore, after filtering the cadmium sulphide, it should be washed with a little sulphuretted hydrogen water, or the sulphuretted hydrogen water added before filtering.

The mechanism of the reaction is practically the same as in the case of hydroxide formation. When the current is passed  $\text{NO}_3$ ,  $\text{Cl}$ , or  $\text{SO}_4$  ions, as the case may be, are liberated at the anode, and oxidise it, causing the metal to pass into solution. At the cathode the reducing action of the hydrogen produces sulphuretted hydrogen, which unites with the salt to produce cadmium sulphide.

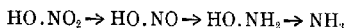
By replacing the cadmium anode by one of other metals, the sulphides of the various metals can be produced.

## **XVI. Hydroxylamine Hydrochloride.**



When nitric acid is reduced in presence of a metallic salt, such as copper sulphate, ammonia is produced, and this reduction may be used as a method for estimating nitrates (p. 145). When, however, the reduction takes place in presence of dilute sulphuric acid

and with a cathode of amalgamated lead, then the nitric acid can be almost quantitatively reduced to hydroxylamine. The nitric acid is probably first of all reduced to nitrous acid, hydroxylamine being the next stage, and the final stage is ammonia. Tafel considers that the ready formation of ammonia, by the reduction of nitric acid in presence of a copper salt (see p. 146), is not due to the formation of  $\text{NH}_2\text{OH}$  and its further reduction, but that the copper exerts a specific influence which prevents the formation of hydroxylamine. Spongy copper or copper sulphate have no action on hydroxylamine, it is therefore probably a question of the effect of the cathode material upon the potential at which the hydrogen is liberated.



The reduction is carried out in an amalgamated circular lead vessel, which acts as cathode. A glass plate is laid on the bottom of the vessel, and on this a porous cell is placed. The anode should consist of a coiled lead tube through which cold water can be circulated. The whole apparatus is then stood in a freezing mixture. The diameter of the cathode should be about 10 centimeters (about 4"), the diameter of the anode cell from 7.0 to 7.5 centimeters (2.75 to 3 inches).

**Amalgamation.**—In order to amalgamate the cathode it must be first carefully cleaned with sand and caustic soda. After this it is washed out with dilute nitric acid, and then thoroughly amalgamated by rubbing it with mercury by means of a rod of wood with a piece of cloth tied on the end.

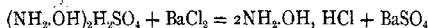
A ring-shaped stirrer made from a piece of lead pipe passes round the outside of the anode cell.

The anode cell is filled about three quarters full with 50-per-cent. sulphuric acid. About 170 to 200 c.c. of acid of the same strength is placed in the cathode compartment. The whole apparatus is now cooled and the circuit closed, a current of about 24 amperes being passed. Twenty grams of nitric acid (30 c.c., 50-per-cent.  $\text{HNO}_3$ ) is then slowly run into the cathode solution

from a dropping funnel: the operation of running in should take about two hours. After all the nitric acid has been run in, the solution is electrolysed for another forty or fifty minutes, until the solution on testing shows only traces of nitric acid.

During the electrolysis the cathode solution should be stirred every few minutes. It is, indeed, better if the stirrer can be fixed on to a rising and falling beam or a slow-moving eccentric, so that the stirring may be continuous.

As soon as the electrolysis is finished the cathode solution is transferred to a beaker, and a warm concentrated solution of barium chloride run in, care being taken, however, that the temperature does not rise above 30° or at most 40°. The barium chloride neutralises the sulphuric acid, and then converts the hydroxylamine sulphate into hydroxylamine chloride.



Care must be taken not to add an excess of barium chloride. The solution is then freed from barium sulphate by filtration, and the clear solution evaporated to dryness on the water bath. If possible, the evaporation should be done in a vacuum, the only difficulty being due to the rather vigorous bumping which often takes place. There is no great difficulty in distilling off the water in a vacuum, provided a good condenser is employed. The residue consists of  $\text{NH}_2\text{OH} \cdot \text{HCl}$  with about 8 per cent. of ammonium chloride. The ammonium chloride can be separated by dissolving the mixture in about half its volume of hot water, when the hydroxylamine salt crystallises out almost pure. The yield of hydroxylamine is from 75 to 80 per cent. of the nitric acid taken.

#### LITERATURE.

J. Tafel, *Zeit. Anorg. Chem.* (1902), **31**, 289.

## CHAPTER XIII.

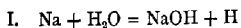
### ORGANIC ELECTROLYSIS.

#### Electrolysis of Organic Acids.

OWING to the very feeble conductivity of organic acids, *i.e.* to the slight amount of ionisation which they undergo, the acids *per se* can only be electrolysed with difficulty, and by the expenditure of a large amount of electrical energy—that is to say, with currents of high potential. On the other hand, the alkaline salts of the acids are fairly good electrolytes, and, therefore, by employing salts of the organic acids, we are able to obtain anionic reactions, the cathodic reactions being of very little importance. The electrodes employed in the electrolysis of the organic acids must be of some material which is unacted upon by the decomposition products or by the oxygen evolved at the anode. Platinum is usually the most satisfactory, although at times graphite or peroxidised lead can be used.

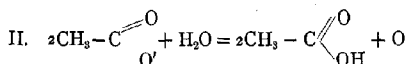
Concentration of the electrolyte, the intensity of current density, and the temperature determine, to a great extent, in what manner the electrolytic decomposition will proceed.

I. In dilute aqueous solution the action is mainly the production of oxygen at the anode and hydrogen at the cathode. The cathode reaction is always the same, and is simply the secondary reaction due to the discharge of the alkali ions; as, for example—



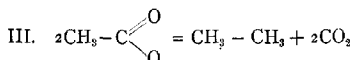
The anode reaction with a dilute aqueous solution of, say, sodium

acetate, is merely a question of oxygen being given up and the acid reformed.

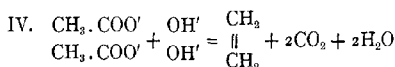


This is the primary reaction which ensues, but secondary reactions may be produced by the oxygen when it is discharged at the anode oxidising the acid itself.

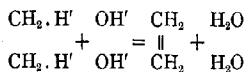
II. With concentrated aqueous solutions the reactions may be much more complicated, and may take place in several ways. One of the most well-known reactions is the preparation of ethane from sodium acetate, in which the carboxyl of the anion is split off, and then two hydrocarbon rests unite together to form ethane.



At the same time small quantities of ethylene are also formed. This must be looked upon as being produced by the decomposition of some of the anions as shown above, and of others as set out below.

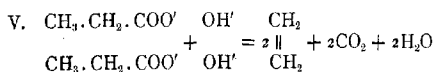


According to the above reaction, it is presumed that, at the moment the  $\text{CH}_3 \cdot \text{COO}'$  ion is liberated at the anode, it splits up into the radical  $\text{CH}_3$  and  $\text{CO}_2$ , and that, before the  $\text{CH}_3$  has time to unite with another  $\text{CH}_3$  radical, two such radicals are attached by hydroxyl groups, which have been simultaneously liberated, with formation of water and ethylene, thus:—

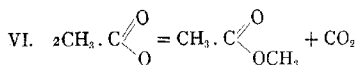


Now, in the case of acetates this reaction only takes place to a very small extent, the main product being ethane produced by

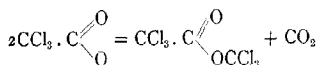
the union of two  $\text{CH}_3$  radicals as in III. With alkali propionates, on the other hand, the main reaction is the formation of ethylene, only a small portion of the  $\text{CH}_3 \cdot \text{CH}_2 \cdot$  radicals uniting to produce butane.



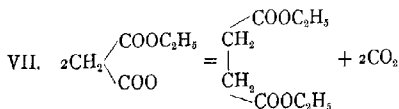
A further reaction may also take place in which one anion splits off  $\text{CO}_2$ , and the alkyl rest so obtained unites with another anion to produce an ester. For example—



A very good example of this class of reaction is illustrated by the formation of the trichlor-methyl ester of trichloroacetic acid when trichloroacetic acid is electrolysed.

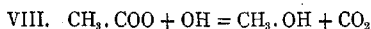


A. Crum Brown and J. Walker, by electrolysing the acid esters of dicarboxylic acids, were able to produce additive compounds, the production of which is made clear by an examination of equation III. As an example, may be given the formation of diethyl succinate when sodium ethyl malonate is electrolysed. Only one of the carboxyl groups is able to take part in the reaction, because the other one is masked by the alkyl group, which prevents it being ionised.

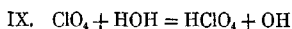


Finally, H. Hofer and M. Moest find that when an organic acid is electrolysed in presence of an alkali sulphate, carbonate, or—

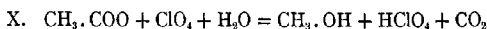
better—perchlorate, that an alcohol is produced. The reaction depends upon the discharge of hydroxyl ions thus—



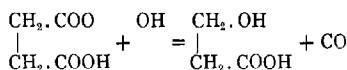
The hydroxyl anion may either be discharged as such, or may be produced by the discharge of the inorganic acid anion, as, for example, with perchloric ions—



We may therefore formulate the production of methyl alcohol by the electrolysis of sodium acetate in presence of sodium perchlorate, as—



The fact that, when an acid is electrolysed in presence of sodium carbonate, an alcohol is produced, explains why it is that on electrolysing a concentrated solution of sodium acetate without a diaphragm, the yield of ethane, which at first is almost quantitative, rapidly falls off. This, therefore, is due to the presence of an alkali carbonate which is produced during the course of the electrolysis, and that, as soon as it is produced, the reaction proceeds according to equation VIII. With dibasic acids, only one of the carboxyl groups is attacked; thus, from succinic acid  $\beta$ -oxypropionic acid is produced.



## XVII. Preparation of Ethane.

A porous cell is fitted tightly with a rubber cork, through which passes a delivery-tube and a piece of stout platinum wire bent in the form of a spiral, and which is intended to function as anode; a piece of sheet platinum may be used instead of the spiral. The porous cell is then filled two-thirds full with a cold saturated solution of sodium acetate, to which is added 1 or 2 per cent. of glacial acetic acid.

The anode cell, round which is coiled a piece of nickel wire to serve as cathode, is placed in a beaker, which is then nearly filled with a similar solution of sodium acetate to that employed for the anode compartment. The whole apparatus is then placed in a vessel of cold water. This form of apparatus can only be employed when it is desired to collect the anode gas alone; if, as is often desirable, it is intended also

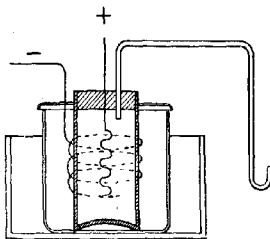


FIG. 57.

to collect the cathode gas, the cell must be placed in a wide-mouthed bottle or a cylindrical glass vessel, and must be fixed air-tight by means of a rubber ring or stopper. The apparatus depicted in Fig. 58 is perhaps the best to employ, when both

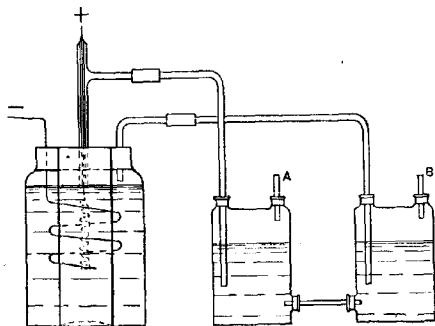
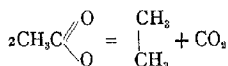


FIG. 58.

gases are to be collected. The two Woolf bottles are employed in order to equalise the pressure on the anode and cathode, the gases being collected from the tubes A and B. Elbs employs a somewhat similar arrangement, in which, however, he uses a tube opening to a bell-shaped end, instead of the porous cell.



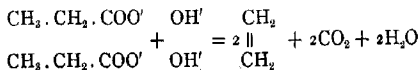
A current density of from 60 to 80 amperes should be employed; this is easily obtained, because the anode surface used is small. The temperature should not be allowed to rise above 20°, because the higher the temperature the lower the yield of ethane. The two wash vessels contain a strong solution of caustic soda to absorb the CO<sub>2</sub> which is produced at the anode, as shown in the equation—



### XVIII. Preparation of Ethylene.

The apparatus and electrodes employed in the preparation of ethylene may be the same as those used in preparing ethane. If, however, the presence of hydrogen with the ethylene is not a disadvantage—as, for example, in the preparation of ethylene dibromide, when the gas is passed through a mixture of bromine and water,—then there is no necessity to separate the anode from the cathode, and the electrolysis can be conducted in a wide-mouthed bottle. The anode is placed in the centre and surrounded with a cylinder of nickel, which acts as cathode. This arrangement has the advantage of decreasing the resistance and of making it easier to keep the apparatus cool. The solution to be electrolysed is prepared by dissolving 40 to 50 grms. of sodium propionate in 100 c.c. of water, and then adding 25 to 30 grms. of propionic acid. When the anode and cathode are separated, a solution of sodium carbonate may be used for the cathode compartment.

The C.D. must, as in the preparation of ethane, be high; it should not be less than 70 amperes, and may rise to 100, provided the temperature of the solution does not rise above 35° or 40°. The yield of the ethylene is between 35 and 50 per cent. of the theoretical amount.



### XIX. Preparation of Diethyl Succinate.

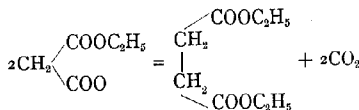
The electrolyte consists of a nearly saturated solution of acid potassium or sodium malonate, which is contained in a beaker standing in cold water. As the hydrogen evolved during the reaction has no action upon the products of electrolysis, it is not necessary to separate the anode from the cathode by means of a diaphragm. The anode should be a spiral of stout platinum wire, and should be sufficiently thick not to become hot when the current is passed. The cathode may conveniently be made of sheet platinum.

#### CONDITION.

C.D. . . . . 50 to 70 amperes.

As the solution is very strong, the electrolyte is rather viscid; and this, and the high current employed, cause very considerable frothing to take place. Therefore the beaker in which the electrolysis is conducted must not be more than half filled with the electrolyte.

After a little while the diethylsuccinate begins to separate out as a mobile oil, which floats upon the surface of the solution. When rather more than the theoretical amount of current has been passed the electrolysis is stopped, the mixture transferred to a separating funnel, diluted with water, and extracted twice with ether. After drying over calcium chloride, the ether is distilled off and the ethyl succinate fractionated; b.p.  $216^{\circ}$ .



For the preparation of potassium ethyl-malonate, see p. 283.

### XX. Preparation of Diethyl Adipic Acid.

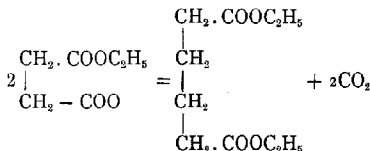
The method of preparation of diethyl adipic acid is similar to that adopted for the preparation of diethyl succinate. A nearly saturated solution of potassium ethyl succinate is electrolysed in a

tall beaker, which, as in the case of the previous experiment, must not be more than half full, owing to the frothing which takes place.

CONDITION.

C.D. . . . . 50 to 75 amperes.

At the end of the reaction—70 c.c. of solution will require the passage of about 20 ampere hours—the mixture with the adipic ester floating upon its surface is diluted with water and extracted twice with ether, and the ethereal solution dried over calcium chloride. After driving off the ether, the oil which remains has a pleasant fruity odour, due to the presence of small quantities of ethyl acrylate,  $\text{CH}_2 : \text{CH} \cdot \text{COOC}_2\text{H}_5$ . In order to free it from this and obtain it quite pure, the ester should be heated to  $120^\circ$  for about half an hour, and then fractionated, b.p. at normal pressure  $254^\circ$ ; but it is more satisfactory to distil under diminished pressure. The yield of ethyl adipic acid is from 30 to 35 per cent. When potassium methyl succinate is electrolysed under the same conditions, dimethyl adipic acid is produced.



For method of preparing potassium ethyl or methyl succinate, see p. 283.

## XXI. Preparation of Methyl Alcohol.

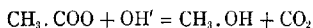
Make up a solution containing 225 grm. potassium acetate, 52 grm. potassium carbonate, and 55 grm. potassium bicarbonate to the litre. In order to prepare methyl alcohol, this solution may either be electrolysed in an undivided cell, or it can be electrolysed in the anode compartment of a partitioned cell.

CONDITIONS.

C.D. . . . . 20–25 amperes.  
 E.M.F. . . . . 7–8 volts.  
 Temp. . . . .  $25^\circ$ – $30^\circ$

The anode should be of platinum, and it is an advantage to have it slowly rotating. As the current density is rather high, the solution is apt to become very hot, and this causes evaporation and loss of the methyl alcohol. For this reason the electrolytic cell should be placed in a basin of cold water, and as a further precaution the cathode should be made from a coil of thin lead piping, on to which is soldered a piece of copper wire to convey the current. Water is caused to flow through the lead pipe, and the coil is placed round the anode compartment, or when the cell is not divided, the lead coil is run close to the outer wall of the electrolysing vessel, the anode being in the centre.

As the electrolysis proceeds, acetic acid is allowed to slowly drop in from a dropping funnel, to take the place of the decomposed acetic ions.



The acetic acid must on no account be run in sufficiently quickly to cause the solution to become acid, otherwise methyl alcohol will not be produced.

When about 50–60 ampere hours of current have been passed, the electrolysis is stopped. The solution containing the methyl alcohol is transferred to a flask, and about one-fifth of it distilled off on a sand bath. The distillate contains the methyl alcohol and traces of formaldehyde. In order to obtain the pure methyl alcohol, small pieces of caustic lime or an excess of anhydrous potassium carbonate is added to the solution, and, after standing for about 24 hours, the flask containing the methyl alcohol and lime is placed on a water bath, and the alcohol distilled off. The yield of methyl alcohol is from 50–60 per cent. There is really no advantage in employing a divided cell, because methyl alcohol is not reduced by the cathodic hydrogen. The weight of the alcohol can be ascertained by multiplying the number of c.c. obtained by 0.789, the specific gravity of methyl alcohol.

#### LITERATURE.

Kolbe, *Annalen*, **69**, 261; Kekule, *Annalen*, **131**, 79; Brazier and Gosleth, *Annalen*, **75**, 265; Murray, *Ber.*, **25**, 492; Hamonet,

*Compt. Rendus*, **123**, 252; Löb, *Zeit. f. Elektrochem.*, **3**, 42; Schall, *Zeit. f. Elektrochem.*, **3**, 83, and **6**, 102; Rohland, *Zeit. f. Elektrochem.*, **4**, 120; Schall and Klien, *Zeit. f. Elektrochem.*, **5**, 256; Elbs, *Journ. f. prakt. Chem.*, **47**, 104; Elbs and Kratz, *Journ. f. prakt. Chem.*, **55**, 502; Troeger and Ewers, *Journ. f. prakt. Chem.*, **58**, 121, and **59**, 464; Aarland, *Journ. f. prakt. Chem.*, **6**, 256; Crum, Brown and Walker, *Annalen*, **261**, 107, and **274**, 41; Walker and Cormack, *Chem. Central Blatt*, **71**, I. 770, and *Proc. Chem. Soc.*, **16**, 58 (1900); Von Miller and Hofer, *Ber.*, **27**, 461, and **28**, 2427; also *Zeit. f. Elektrochem.*, **4**, 56; Hofer, *Ber.*, **33**, 650; Hofer and Moest, *Annalen*, **323**, 304 (1902); Moest, *D.R.P.*, 138,442 (1903); Foerster and Piquet, *Zeit. f. Elektrochem.*, **X**, 729 (1904); Hofer and Moest, *Zeit. f. Elektrochem.*, **10**, 833 (1904).

## CHAPTER XIV.

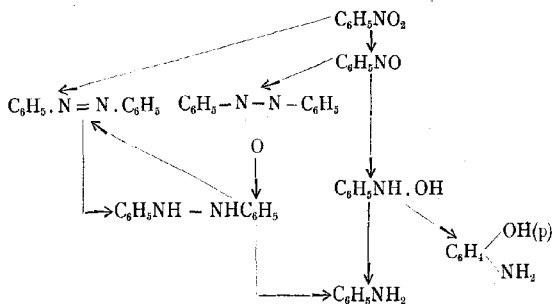
### REDUCTION OF ORGANIC COMPOUNDS.

THE electrolytic reduction of organic compounds has been very fully studied, and the results obtained have been of great importance. Compared with methods of electrolytic oxidation those of reduction are comparatively easy. Very different results can be obtained by varying the conditions of reduction. Thus, for example, different reduction products are obtained from the same substance by reducing in strong acid or dilute acid solutions, in alkaline or neutral solutions. The material of the electrode also has a considerable influence upon the manner of the reduction. This is not due to the difference of the metal, but to the fact that with certain metals the hydrogen is yielded up at a higher potential. In fact, the chief influence in the reduction is the potential at which the hydrogen ions are discharged. W. Löb and R. W. Moore<sup>1</sup> find that nitrobenzene can be reduced in alkaline solution with a cathode of platinum, copper, tin, zinc, lead, or nickel, or with a platinum cathode and the hydroxide of tin, zinc, or lead.

In general chemistry it is well known that when nitrobenzene is reduced in acid solutions aniline is produced, but reduction in alkaline solution leads to the formation of azoxybenzene, azobenzene and hydrazobenzene. The electrolytic reduction of nitrobenzene and of substituted compounds of nitrobenzene has been very thoroughly studied, and it is found that it is possible to bring about by electrical means the same changes as those produced by purely chemical methods, and very

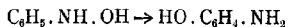
<sup>1</sup> *Zeit. f. Phys. Chem.*, (1904), 47, 818.

often with very much greater readiness. Some of the reactions are due to primary electrolytic reduction, but others must be classed as being brought about by secondary changes. F. Haber<sup>1</sup> has drawn up a scheme in order to show this in a clear manner. In the scheme, here given, the vertical arrows show the primary changes, and the oblique indicate secondary reaction.



## REDUCTION IN ACID SOLUTION.

The primary reaction from nitrobenzene to nitrosobenzene, phenylhydroxylamine, and aniline takes place in moderately dilute acid solution. When strong acid is employed, the main product is p-amidophenol. In strong sulphuric acid phenylhydroxylamine undergoes intramolecular change, the OH group exchanging place with a hydrogen atom in the para-position thus :—



## XXII. Preparation of Aniline.

25 grm. of nitrobenzene is dissolved in 100 c.c. of alcohol, and added to 200 c.c. of sulphuric acid (25 to 30 per cent.). This mixture is placed in a porous cell which acts as cathode chamber. The cathode is made of a sheet of lead bent into the form of a

<sup>1</sup> *Zeit. f. Elektrochem.* (1898), 4, 506.

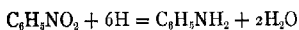
cylinder, and having narrow slots cut into it at intervals. A small lead paddle, also connected with the negative pole of the source of current, is placed in the centre of the cell, and rapidly rotated during the time the electrolysis is being conducted. If the mixture is not agitated, sufficient alcohol should be employed to keep the nitrobenzene almost completely in solution, and the cathode solution is placed in a high beaker, the porous pot containing the anode.

The anode may be a cylinder or sheet of lead, the anode solution sulphuric acid of the same strength as that employed for the cathode solution.

## CONDITIONS.

C.D. . . . .	4 to 5 amperes.
E.M.F. . . . .	3.7 to 4.0 volts.
Temp. . . . .	65° to 80°

The electrolysis is commenced at normal temperature, but the passage of the current rapidly raises the temperature to the boiling point of alcohol. The object of the high beaker is to condense as far as possible the alcohol which is vaporised by the high temperature. From the equation it is seen that 123 gm. of nitrobenzene require the passage of six faradays or  $6 \times 96540$



coulombs of electricity in order to reduce it to aniline. Therefore 25 gm. require about 33 ampere hours. As toward the end of the reaction a certain quantity of hydrogen is invariably lost, the current should be passed for about 35 ampere hours.

The alcohol is now distilled off, the solution made alkaline with caustic soda, and steam distilled. If there is a trace of nitrobenzene left, this can be separated by a preliminary steam distillation before making alkaline. The aqueous distillate is extracted with ether, and the aniline recovered as usual. Yield about 80 per cent. or higher. Crystals of aniline sulphate can be obtained by evaporating the acid solution to small bulk, but there is no advantage in this.



### Toluidines.

Ortho- meta- and para-nitrotoluene are readily reduced in a similar manner to nitrobenzene with a formation of the corresponding toluidines. The yields of toluidines are very satisfactory, but the o- and m-nitrotoluenes give rather higher yields of the corresponding toluidines than the p-nitro-toluene.

### XXIII. Preparation of p-Amidophenol.<sup>1</sup>

As has already been stated (p. 236), p-amidophenol is obtained when nitrobenzene is reduced in strong solutions of sulphuric acid. The strong acid causing an intra molecular change between the OH group of the hydroxylamine and the hydrogen atom situated in the para-position.

Owing to the strong sulphuric used, and the high temperature at which the reaction is conducted, platinum electrodes must be employed. The anode and cathode are separated; either an ordinary porous cell may be used, or one of the double perforated cells (p. 196), in which the inner portion is wrapped round with asbestos, can be employed.

30 grm. of nitrobenzene is mixed with 200 c.c. of strong sulphuric acid, and about 4 to 6 c.c. of water added. This solution is placed in a beaker which constitutes the cathode space; the anode compartment, which has first been soaked in strong sulphuric acid, is placed in the middle of the beaker. A spiral of thick platinum wire, which forms the cathode, is wound loosely round the anode cell, or a cylinder of platinum may be used instead of wire. The anode may either be a cylinder of platinum foil or, better, a stout coil of platinum wire.

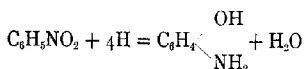
#### CONDITIONS.

C.D. . . . .	5 to 6 amperes.
E.M.F. . . . .	7 to 8 volts.
Temp. . . . .	75° to 80°

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<sup>1</sup> Gattermann, *Ber.*, **20**, 1846. A. Noyes & A. Clement, *Ber.*, **28**, 990.

No heating is required, but during the reaction the temperature rises to 75° or 80°. It must not be allowed to exceed 85°, otherwise sulphonation takes place, and p-amidophenol sulphonate is produced; even at this lower temperature a certain amount of sulphonation does ensue. As the electrolysis proceeds, the solution becomes of a dark-blue colour. After about 30 ampere hours of current have passed the reduction is stopped, and the



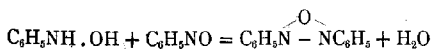
anode cell removed. On allowing to stand for some time in a cool place or by placing the beaker in a freezing mixture the p-amidophenol crystallises out, the whole mass becoming a thin porridge of crystals. The crystals are filtered off on the filter pump, glass wool or asbestos being used to filter through. After filtration, the crystals are spread on a piece of porous plate to remove as much of the sulphuric acid as possible, and recrystallised from alcohol. The yield is generally about 20 to 30 per cent., but if the temperature has been allowed to rise too high, it may be very much lower. There is always a certain quantity of the sulphonic acid formed, and varying quantities of higher reduction products. When 80-per-cent. sulphuric acid is used, less sulphonation takes place, but in this case the cathode must be rapidly rotated.

## REDUCTION IN ALKALINE SOLUTION.

In alkaline solution the reactions are mostly secondary; according to Haber's scheme (p. 236), it is seen that azoxy and azo compounds are produced. The formation of the azoxy compounds may be written as :—



It probably is also produced as a secondary reaction between phenylhydroxylamine and nitrosobenzene.



The nitrobenzene is first reduced to nitrosobenzene, a portion of which is then further reduced to phenylhydroxylamine, and the interaction of these two substances causes the formation of the azoxybenzene.

#### XXIV. Preparation of Azoxybenzene.<sup>1</sup>

As cathode compartment use a fairly wide porous cell about 8 or 9 cm. in diameter, and place it in a cylindrical lead vessel, which is to serve as anode. The anode solution is a 15-per-cent. solution of sodium sulphate slightly acidified with sulphuric acid.

Mix 30 grm. of nitrobenzene with 300 to 400 c.c. of 3-per-cent. solution of sodium hydrate, and place the mixture in the cathode cell. The cathode may consist of a nickel gauze cylinder or a close coil of stout nickel wire, wound so as to fit closely against the walls of the cathode cell. A nickel stirrer is then placed in the centre of the cell, and the mixture is vigorously agitated so as to produce a thorough emulsion, the nickel stirrer being also connected with the negative source of current.

##### CONDITIONS.

C.D. . . . .	5 to 6 amperes.
E.M.F. . . . .	6 to 8 volts.

No external heat is applied, but during the electrolysis the temperature of the solution rises considerably.

According to the equation already given, two molecules of nitrobenzene are seen to require about 33 ampere hours of current, therefore 30 grm. theoretically should need 16.5 ampere hours. It will be found advisable to give the experiment about 22 ampere hours. Shortly after the current has been passed the solution becomes bright red, but towards the end of the reaction the solution often appears rather muddy and of a brownish red colour.

After the electrolysis is finished, the mixture is transferred to a flask and steam distilled to remove unchanged nitrobenzene and

<sup>1</sup> *Chem. Zeit.*, 17, 210.

any aniline which may have been formed. As the azoxybenzene is also to a certain extent volatile with steam, the distillation must be stopped when the distillate only smells faintly of nitrobenzene—that is, after 30 or 40 minutes' distillation. The bulk of water is poured off the oil which remains at the bottom of the distillation flask, and the oil poured into a beaker. On standing for some little time in a cool place the oil solidifies. The crude azoxybenzene is purified by recrystallisation from petroleum ether or from ligroin. It is obtained as crystalline plates or needles of a light yellow colour; m.p.  $36^{\circ}$ . The yield varies considerably, but is not usually above 40 per cent.

Very little work appears to have been done upon the nitrotoluenes, but p-azoxytoluene has been prepared by electrolytic reduction of p-nitrotoluene with a C.D. of 1 to 2 amperes. It is a red sandy substance which on crystallisation from alcohol forms orange-red needles, m.p.  $75^{\circ}$ .

## XXV. Preparation of Azobenzene.<sup>1</sup>

When the reduction is carried a stage further than is necessary for the formation of azoxybenzene, azobenzene is produced.



Dissolve 30 grm. of nitrobenzene in 200 c.c. of 70-per-cent. alcohol, and add 8 grm. of sodium acetate: this solution forms the cathode mixture. Place it in a narrow beaker, and as anode compartment use a porous cell. The anode solution consists of a cold saturated solution of sodium carbonate. The anode may be of platinum foil or wire, or a graphite rod can be employed. The cathode should be a nickel gauze cylinder, placed between the anode cell and the beaker.

### CONDITIONS.

C.D. . . . .	6 to 8 amperes.
E.M.F. . . . .	8 to 9 volts.
Temp. . . . .	Normal to commence with,

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K. Elbs and O. Kopp, *Zeit. f. Elektrochem.*, 5, 108.

R

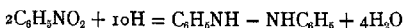
but as the electrolysis proceeds the mixture rapidly reaches the boiling-point of the alcohol. The object of having a tall narrow beaker is to condense, as far as possible, the volatilised alcohol; it may, however, be necessary to add fresh quantities of alcohol from time to time. Toward the end of the reaction the C.D. is reduced to 2 amperes, and the current passed for about  $1\frac{1}{2}$  hours at this density. About 30 ampere hours are required to complete the reduction—that is, the passage of slightly more than the theoretical amount of current. As a high C.D. is being used, and because during the electrolysis the anode solution tends to become depleted of cations, the anode cell should not be too small, as otherwise, owing to resistance being set up, a high E.M.F. is required to drive the current through, and the heating of the solution becomes excessive.

As soon as the process is finished, the mixture is transferred to a flask, and air is aspirated or blown through it for about half an hour. The object of passing air through the mixture is to decompose any hydrazobenzene which may have been produced, as it is found that a small quantity of this product is invariably formed. Traces of azoxybenzene may also be present. The bulk of the alcohol is distilled off, excess of water added, and the precipitated azobenzene filtered off and washed. If the reduction has not been carried far enough, the unchanged nitrobenzene remaining makes it very difficult to get the azobenzene to crystallise. The only thing to do in this case is either to further reduce the product or to steam distil it, but this latter method always results in loss, because some of the azobenzene passes over with the steam. It is then recrystallised from alcohol or light petroleum spirit, when it is obtained in beautiful red plates; m.p.  $68^{\circ}$ . Yield about 70 to 75 per cent.

## XXVI. Preparation of Hydrazobenzene.<sup>1</sup>

From the equation for the formation of hydrazobenzene, it is seen that two more hydrogen atoms are required to produce it than are necessary for the preparation of azobenzene.

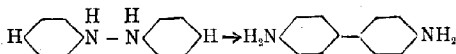
<sup>1</sup> K. Elbs and O. Kopp, *Zeit. f. Elektrochem.*, 5, 108.



In preparing hydrazobenzene, the conditions of the experiment, solution, electrodes, etc., is the same as in the previous case. For 30 grm. of nitrobenzene theoretically about 32 ampere hours are required, but to ensure complete reduction the current should be passed for about 35 ampere hours. After sufficient current to produce azobenzene has been passed, the C.D. should be dropped to 2 or 3 amperes—say, *e.g.*, after the passage of 25 ampere hours. As the reduction becomes completed, crystals of hydrazobenzene commence to fall out; when the process is completed, the beaker containing the product is placed in a basin of cold water, and a low current of 0.5 to 0.75 ampere passed while the substance is cooling, say for three-quarters of an hour. The bulk of the hydrazobenzene thus crystallises out, and, on rapidly filtering on the pump and washing, first with dilute acetic acid, and then with alcohol, the hydrazobenzene is found to be practically pure. Another crop of crystals can be obtained from the mother liquors by addition of water containing a little ammonium sulphide—to prevent oxidation. This last portion can be obtained quite pure by recrystallisation from alcohol. Hydrazobenzene forms colourless tablets; m.p.  $131^\circ$ ; yield over 80 per cent.

## XXVII. Preparation of Benzidine.<sup>1</sup>

When hydrazobenzene is acted upon by strong sulphuric acid it is converted by intramolecular change into benzidine, as shown by the following scheme :—



This preparation can hardly be called an electrolytic one, but as it is very readily produced from hydrazobenzene, it is included here. In order to prepare it, the cathodic mixture is after electrolysis, without cooling, poured into moderately strong hot sulphuric acid (200 c.c.  $\text{H}_2\text{SO}_4$ , 400 c.c.  $\text{H}_2\text{O}$ ).<sup>1</sup> This must

<sup>1</sup> W. Lob, *Zeit. f. Elektrochem.*, 7, 320 and 333, also 597.

be done with caution, because the solution containing the hydrazobenzene is strongly alkaline, and when it is poured into the hot acid, unless care be taken, the reaction becomes too violent. In order to prevent reduction of the hydrazobenzene it is advisable to add a few crystals of sodium sulphite to the cathode solution before pouring it into the sulphuric acid. The benzidine sulphate separates out as a crystalline powder, and, after cooling, this is separated off. In order to remove any azobenzene which may be present, owing to oxidation, it is washed with warm alcohol. About 65 per cent. of the theoretical amount of benzidine sulphate is produced. The free base is obtained by grinding up the benzidine sulphate in a mortar with excess of ammonia. The base is then filtered off and washed with a little cold water to remove the ammonium sulphate, and the benzidine crystallised from boiling water. As it is not very soluble in water, a considerable quantity is required to dissolve it. On cooling, large colourless plates or leaflets are obtained, which are filtered off and washed with a little water and dried. m.p.  $122^{\circ}$ .

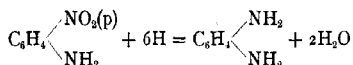
The azo- and hydrazo-compounds of other nitro-compounds are readily prepared by the same methods as those used for preparing these compounds from nitrobenzene. Thus the azoxy compounds obtained from p-nitro-anisol and from the nitroxylens are really easier to prepare than ordinary azoxy and azobenzene, because they melt at much higher temperatures and are therefore more readily crystallised. Other substituted azoxy and azobenzenes can be produced by employing substituted nitrobenzenes. For example, the three chloronitrobenzenes yield the corresponding chloroazoxybenzenes, etc.

### XXVIII. Preparation of p-Phenylenediamine.<sup>2</sup>

By reduction of the ortho- and para-nitraniline the corresponding diamines are readily obtained; *e.g.* with p-nitraniline—

<sup>1</sup> Commercially hydrochloric acid is generally employed instead of sulphuric acid.

<sup>2</sup> A. Noyes and J. J. Dorrance, *Ber.*, **28**, 2350.



Take 20 grm. p-nitraniline and dissolve in about 150 to 200 c.c. of alcohol; now dissolve 5 to 7 grm. sodium acetate in 100 c.c. of hot water, and mix the two solutions. This mixture is then placed in a beaker, which acts as the cathode cell. The cathode is of nickel gauze, as also is the anode. The anode cell is filled with a 20-per-cent. solution of sodium carbonate.

## CONDITIONS.

C.D. . . . .	14 to 18 amperes.
E.M.F. . . . .	7 to 8 volts.
Temp. . . . .	75° to 80°

The mixture is made warm to start with; the high current used keeps it at the boiling-point of the alcohol. The evaporated alcohol may be replaced from time to time.

After the passage of 24 ampere hours the current is stopped. The first 18 or 20 ampere hours of electricity are passed at a high current density, then the current is gradually cut down to 2 amperes.

At the end of the reaction the still hot cathode fluid is poured into a mixture of 50 c.c. sulphuric acid and 100 c.c. water. The mixture is allowed to stand for an hour or two, filtered on the pump, and then spread on a porous plate. By this means colourless plates of p-phenylenediamine sulphate are obtained. The yield is about 75 per cent. of the theoretical quantity obtainable.

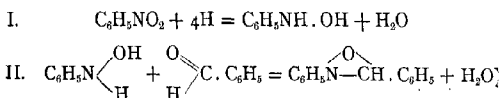
It should be noticed that whereas o-nitraniline upon reduction in the above manner yields o-phenylenediamine, m-nitraniline yields, when reduced under similar conditions, m-diamidoazobenzene. This peculiarity is due to the tendency of the ortho- and para-compounds to form quinones, a tendency which is not exhibited by the meta compounds.



## REDUCTION OF A MIXTURE OF NITROBENZENE AND BENZALDEHYDE.

### XXIX. Preparation of Benzyldenephényl- hydroxylamine.<sup>1</sup>

The preparation of benzyldenephénylhydroxylamine by the reduction of nitrobenzene in presence of benzaldehyde is of considerable theoretical importance, because it proves that phenylhydroxylamine is a product of the reduction of nitrobenzene, and that aniline is produced by its further reduction. The reactions which take place in the preparation of benzyldenephénylhydroxylamine may be written in two stages.



The cathode mixture consists of 18 grm. nitrobenzene and 20 grm. benzaldehyde dissolved in 40 grm. of glacial acetic acid, to this solution 40 grm. (about 22 c.c. of concentrated sulphuric acid) is added. The mixture is poured into a beaker, which acts as cathode compartment.

The anode solution is made up of 3 parts concentrated sulphuric acid and 1 part water, and is placed in a porous cell which stands in the beaker.

Both anode and cathode must be made of platinum. Stout platinum wire is the most satisfactory form to employ for the anode. The cathode may either consist of platinum wire coiled loosely round the anode cell, or, better, a cylinder of platinum—for example, a cylinder such as is employed in electrolytic analysis.

#### CONDITIONS.

C.D. . . . .	4 to 5 amperes.
E.M.F. . . . .	5 to 7 volts.
Temp. . . . .	18° to 20°

<sup>1</sup> Gattermann, *Ber.*, 29, 3040.

The whole apparatus is placed in a vessel of cold water to prevent the temperature rising above about 20°.

The amount of current necessary to reduce 18 gram. of nitrobenzene to phenylhydroxylamine is 15.5 ampere hours, but in order to obtain a good yield of benzylidenepherylhydroxylamine it is found necessary to pass the current for more than double this time, about 35 ampere hours.

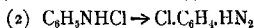
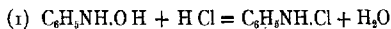
When the requisite amount of current has been passed, the electrolysis is interrupted, and the contents of the cathode vessel poured upon ice or into ice-cold water. The crystalline product so obtained has usually a brownish or reddish-brown appearance, and often contains small quantities of oil, due to undecomposed nitrobenzene or benzaldehyde. The substance is first washed with water, then with dilute alcohol, and finally crystallised from alcohol, by which means colourless needle-shaped crystals are obtained; m.p. 108° to 109°. Yield about 60 per cent.

### XXX. Preparation of Ortho- and Para-chloroaniline.

On p. 238 it has been found that when nitrobenzene is electrolysed in a strong solution of sulphuric acid that the phenylhydroxylamine which is produced in the second stage of the reduction is converted by intramolecular change into p-amidophenol. On electrolysing a mixture of nitrobenzene and strong hydrochloric acid, intramolecular change also takes place, but with production of chloroanilines, the change which takes place may best be shown as follows:—



In presence of strong hydrochloric acid the phenylhydroxylamine is converted into phenylchloramine, which then undergoes intramolecular change, a portion of the chlorine changing places with the hydrogen atom in the ortho position, and a part with the hydrogen atom in the para position, thus:—



**Process.**—A small porous pot, capable of holding 200 to 250 c.c., which should not be less than from 5 to 6 cm. in diameter, is employed as cathode compartment. The cathode may either be a cylinder of platinum or a fairly close coil of platinum wire, wound so as to come against the sides of the porous cell. In the centre of the cell there should be placed a small stirrer of stout platinum wire to which has been welded a piece of thick platinum foil, to act as a paddle. The cathode solution is made by suspending 35 grm. of nitrobenzene in 175 to 200 c.m. of the strongest hydrochloric acid. The cell is then placed in a beaker filled with dilute sulphuric acid (20 per cent.). Platinum foil or wire may be used for the anode. Before commencing the reduction, the stirrer, which should be rotated sufficiently rapidly to create a good emulsion, is started, and the current then switched on.

#### CONDITIONS.

C.D. . . . .	1'5 to 2 amperes.
E.M.F. . . . .	5 to 6'5 volts.

It is necessary to pass the current for considerably longer time than is theoretically required, 45 to 50 ampere hours being used instead of 30 ampere hours, the theoretical amount. If, however, the smell of nitrobenzene is no longer noticed, the electrolysis can be stopped when less current than above mentioned has been passed. The solution in the porous pot has a greenish colour, and it will be found on pouring it into a beaker that a small quantity of greenish precipitate is suspended in it; filter this off. Now evaporate the solution nearly to dryness on the water bath; on cooling, crystals separate out. Add sufficient water to dissolve these crystals and then excess of caustic soda; at first a precipitate forms, but this rapidly changes into a violet-coloured oil. This mixture is then steam-distilled, an almost colourless oil being obtained in the receiver (a certain quantity of a violet-coloured oil remains in the distilling flask). The distillate is extracted with ether, dried over

calcium chloride, and the ether distilled off. The oily substance which remains after this treatment is a mixture of ortho- and p-chloroaniline.

**Separation of Ortho- and Para-chloroaniline.**—The oily mixture is boiled with acetic anhydride, whereby the acetyl compounds are obtained. The anilides are then washed free from excess of acetic anhydride, dried and boiled for some time with a considerable excess of benzene in a flask fitted with a reflux condenser. The o-chloroaniline dissolves, and a small portion of the para-compound. The benzene solution is filtered off, and, on cooling, crystals separate out; these consist of the dissolved para-compound. After separating these crystals the benzene solution is distilled off, an oil being obtained which rapidly solidifies; this is the ortho-compound: m.p.  $87^{\circ}$ . The acetyl-p-chloroaniline melts at  $172^{\circ}$  to  $173^{\circ}$ .

If desired to prepare the pure bases from the acetyl compounds, this can be done by heating in a closed tube with hydrochloric acid to a temperature of  $180^{\circ}$ . The solution so obtained is then made alkaline and steam-distilled. The boiling-point of the ortho-compound is  $206^{\circ}$ , while the p-chloroaniline melts at  $71^{\circ}$  and boils at  $231^{\circ}$ .

The reaction does not go completely in the manner set out in the equations, because there is always 20 per cent. or more of the nitrobenzene converted into a violet-coloured oil. This oil, the constitution of which has not yet been determined, is left behind in the flask when the ortho- and p-chloroaniline are steam-distilled.

## REDUCTION OF SUBSTANCES CONTAINING THE KETO GROUP.

In the reduction of substances containing the carbonyl group  $>CO$ , the nature of the cathode is, as Tafel<sup>1</sup> has shown, of very great importance. With platinum electrodes, generally speaking,

<sup>1</sup> *Ber.*, 33, 2209.

very little reduction takes place, the most powerful effects being produced when lead cathodes are employed. When lead is used as cathode the hydrogen ions are discharged at a higher potential than when other metals are employed. In fact, the presence of only very small quantities of foreign metals seems to considerably lower this over-potential. From his experiments, Tafel draws the following conclusion:—" *That substances which are difficult to reduce can only be reduced in sulphuric acid solution when such cathodes are employed which give a particularly high over-potential at the cathode.*"

Furthermore, the concentration of the acid is of importance; but the best results are obtained with solutions of a concentration between 30 and 60 per cent. With very strong sulphuric acid, the acid itself becomes reduced, and sulphur is thrown out.

Another point of importance is the current density—generally speaking, *the lower the current density the more rapid and complete the reduction.* This, of course, means the employment of a large cathode surface.

During the reduction, it is often advantageous to add small quantities of lead acetate solution (about 0.5 c.c. of a normal solution of lead acetate); this is to counteract the influence of small quantities of metallic impurities which may be present.

### Preparation of Lead Electrodes.

The lead should be as pure as possible, but it is not absolutely essential that it should be chemically pure. No soldered

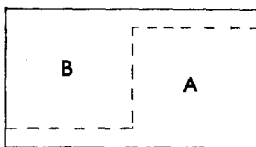


FIG. 59.

electrode B has a long narrow piece of metal, at the end of which a piece of copper wire can be soldered. The electrode A

joints may come near to the electrolysing cell. The best way to cut the lead is shown in Fig. 59; by cutting in this manner, two electrodes can be obtained from each piece of sheet lead. The

has a similar extension on which the copper connection may be fixed. The electrodes can then be bent into any desired form.

In order to prepare the surface of the electrode, it is well rubbed with sand and water, washed with caustic soda, and again rinsed with water. It is then placed in a vessel of 20-per-cent. sulphuric acid, in which it is made the anode, and a current of 2 amperes per square decimeter passed for about half an hour. The surface of the electrode is now covered with a coating of lead peroxide. It is then washed under the tap, and placed into boiling water for a few minutes, and finally it is dipped into alcohol and then dried by means of a blast of air. The electrode is now ready for use.

The first action of the current, when this electrode is made the cathode, is to reduce the peroxide coating and to cover the surface of the electrode with a thin membrane of spongy lead. Even if the lead in the first case was not quite pure, this treatment goes a long way towards improving its purity, and further hydrogen given off on the surface of spongy lead appears to be given up at a higher over-voltage than from a polished lead surface.

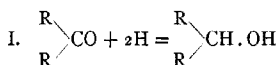
It is advisable to oxidise the electrode each time before employing it in a new experiment.

### **Preparation of Porous Cell.**

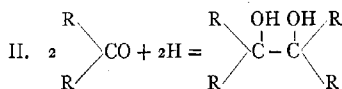
The porous cells often contain more or less metallic impurities; they must also be carefully purified. This is done by first soaking them in a warm dilute solution of caustic soda for a few hours, and then placing them in boiling distilled water for another few hours; after which they are soaked in dilute hydrochloric acid over-night—Tafel recommends for several days; finally soaked for a day or two in distilled water, which should be changed every now and then.

## REDUCTION OF SUBSTANCES CONTAINING THE KETONE (CARBONYL GROUP).

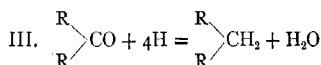
When a substance containing the carbonyl group is reduced, there are three possible changes which may take place. In the first place, a secondary alcohol may be produced—



Or two molecules may condense together with formation of a pinakone.



Or, thirdly, the oxygen atom may be eliminated with formation of water, the place of the oxygen being taken by two atoms of hydrogen.



When acetone is reduced with a mercury cathode, the electrolyte being dilute sulphuric acid, then reaction I. takes place, and isopropyl alcohol is produced. When, however, it is electrolysed with lead or other insoluble electrodes, the electrolyte being the same, the reaction goes partially according to I. and partially according to II., so that a mixture of isopropyl alcohol and pinacone is obtained.

### XXXI. Preparation of Isopropyl Alcohol.<sup>1</sup>

The cathode solution is prepared by dissolving 20 gm. acetone in 100 c.c. of 40-per-cent. sulphuric acid. The anode solution

<sup>1</sup> Tafel, *Zeit. f. Elektrochem.* (1902), 8, 288.

is 10-per-cent. sulphuric acid, and the anode may be a piece of compo-pipe to which a copper wire is soldered. The apparatus employed is depicted in Fig. 60. It consists of a glass cell, the bottom of which is covered with a layer of mercury, A, about 1 to 2 c.m. deep. B is a piece of stout platinum wire which passes through a glass tube to the bottom of the vessel, and makes electrical connection with the mercury. The porous cell c is clamped in such a way that it is about 5 c.m. above the surface of the mercury. In order to keep the mixture cool during electrolysis, the whole apparatus is

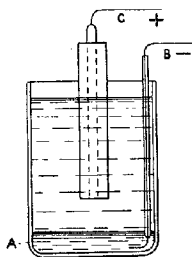


FIG. 60.

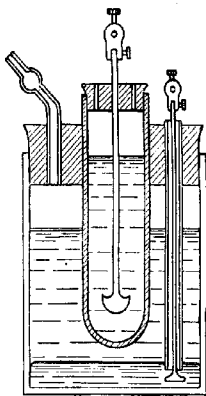


Fig. 61.

placed in a vessel of cold water. Tafel recommends the apparatus shown in Fig. 61. The advantage of Tafel's apparatus is that it allows the collection of the cathode gases, so that one is able to follow the course of the reduction, and it is easy to find out how much of the hydrogen is used for reduction and how much is unused.

In order to ascertain the C.D., it is, of course, necessary to know the surface of the mercury; this is readily found by measuring the diameter of the electrolysis cell.

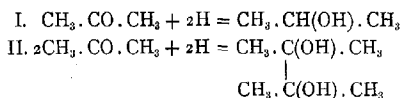
If a current of 4 amperes is passed, the electrolysis will be complete in about 10 hours. When much higher currents than this are employed, it is sometimes rather difficult to keep the solution sufficiently cool.



As soon as the reduction is completed the clear cathode solution is neutralised with solid caustic potash, care being taken not to allow the temperature to rise above  $25^{\circ}$  or  $30^{\circ}$ . As soon as the mixture is slightly alkaline, excess of anhydrous potassium carbonate is added, the mixture transferred to a flask and distilled from the water bath. The isopropyl alcohol which passes over is dried with a little anhydrous potassium carbonate and fractionated, when almost the whole of it passes over between  $80^{\circ}$  and  $81^{\circ}$ . The yield is about 18 to 19 grm.

### XXXII. Preparation of Isopropyl Alcohol and Pinacone.<sup>1</sup>

In order to prepare isopropyl alcohol and pinacone at the same time, the only difference from the last experiment is in the material of the electrode, which is lead. The best form of apparatus is a small lead vessel, which is used as cathode; the anode may be also of lead, and is placed as before in a porous cell. A current density of 4 amperes per square decimeter is employed, and the solution is kept cool by placing the lead vessel into a basin through which cold water is circulated. The following equations both take place concurrently:—



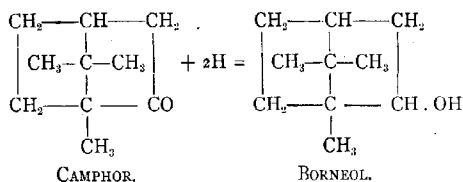
As soon as the reaction is completed, which can be told from the vigorous evolution of hydrogen, the clear solution obtained is treated with caustic potash until slightly alkaline, and then with excess of anhydrous potassium carbonate; the mixture is, however, not directly subjected to distillation, as in the last experiment. The addition of the excess of potassium carbonate causes the formation of two layers, the lower one being a concentrated aqueous solution of potassium carbonate. This is separated from the upper layer, which consists of a mixture of

<sup>1</sup> E. Merck, *D.R.P.*, 113,719 (1893).

isopropyl alcohol and pinacone. The two substances are now readily separated by fractionation. The boiling-point of isopropyl alcohol is  $80^{\circ}$  to  $81^{\circ}$ , that of pinacone  $171^{\circ}$  to  $172^{\circ}$ . With water pinacone forms a crystalline hydrate  $(\text{CH}_3)_2\text{C}(\text{OH}) \cdot \text{C}(\text{OH})(\text{CH}_3) + 6\text{H}_2\text{O}$ ; m.p.  $42^{\circ}$ . The anhydrous pinacone melts at  $33^{\circ}$ .

### XXXIII. Preparation of Borneol.<sup>1</sup>

Camphor also contains the keto group, and on reduction yields the secondary alcohol borneol.



The cathode may be a lead vessel, all the joints of which must be burnt and *not* soldered. This vessel is prepared in the manner already described for lead electrodes (p. 251). The anode should be a piece of pure sheet lead, and is placed in a porous cell, which stands upon a piece of glass placed on the bottom of the cathode cell. Or it may be held about 5 cm. from the bottom of the vessel by means of a clamp. The cathode solution is prepared by dissolving 10 gm. of camphor in 100 to 120 c.c. alcohol, and then adding 60 to 100 c.c. of 75-per-cent. sulphuric acid. If the camphor is precipitated out, a further quantity of alcohol must be added. The anode solution may be 70-per-cent. sulphuric acid. In order to prevent the mixture becoming hot during the electrolysis, the lead cell is placed in a vessel through which cold water is circulated.

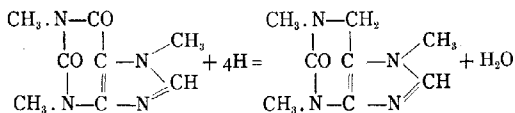
With a current of 3 amperes the reduction is finished in ten hours. The C.D. may be from 10 to 12 amperes, so that if the cathode surface is  $\frac{1}{2}$  square decimeter, then a current of 6 amperes

<sup>1</sup> J. Tafel and K. Schmitz, *Zeit. f. Elektrochem.* (1902), 8, 288.

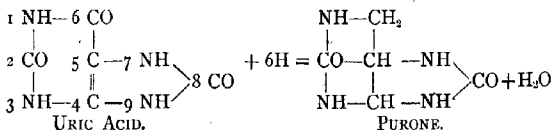
may be employed, provided the temperature does not rise above  $20^{\circ}$  to  $24^{\circ}$ , and in this case the reduction would be finished in five hours. The electrolyte does not conduct the current very well, therefore the E.M.F. will be found to be from 10 to 15 volts, although it may fall considerably toward the end of the reaction.

When the electrolysis is finished the cathode mixture is poured into a beaker, when it will be found to separate into two layers. Excess of water is now added, and a semi-crystalline mass obtained; this is extracted with ether; the ethereal solution is washed and dried and the ether distilled off. The crystalline mass so obtained is then purified by recrystallisation from ligroin. The m.p. of the pure product is  $204^{\circ}$  to  $205^{\circ}$ , and the yield from 42 to 45 per cent.

The third form of reduction (p. 252), where the keto group is converted into the  $\text{CH}_2$  group, takes place, as has been shown by Tafel, when caffeine is electrolytically reduced, desoxycaffeine being produced; thus :—



This form of reduction also takes place when uric acid is reduced, purone being formed :—



The reduction here, however, is not confined to the replacement of the oxygen of the 6 carbonyl group, but goes a step further, and also reduces the double-bonded carbon atoms 4 and 5. It is an interesting fact that until Tafel succeeded in electrolytically reducing uric acid, all attempts at its reduction had failed.

Tafel finds the above reaction, in which the carbonyl group is reduced to the  $\text{CH}_2$  group, to be general; alkyl xynthines and alkyl derivatives of uric acid are also reduced in a similar manner.

The preparation and purification of purone presents considerable difficulties, whereas the reduction of caffeine is comparatively easy; the preparation of desoxycaffeine is therefore given as an example of this class of reduction.

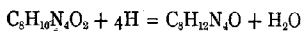
### XXXIV. Preparation of Desoxycaffeine.<sup>1</sup>

Fifteen gm. of caffeine is dissolved in a mixture of 22 c.c. concentrated sulphuric acid and 40 c.c. water. This solution is placed in a beaker, inside which there is a small porous cell which has previously been soaked in 50-per-cent. sulphuric acid, the anode solution consisting of sulphuric acid of this strength. The anode is a piece of lead sheet, or of lead pipe. The cathode is made of lead sheet, which has previously been prepared as described on p. 251, and is bent in the form of a cylinder, so as to surround the anode cell. The whole apparatus is placed in a bath of cold water. A carefully prepared lead vessel may be used instead of the beaker for holding the cathode solution; in this case, of course, the lead vessel acts as cathode. Or the cathode solution may be placed in the porous cell, and the lead vessel made the anode.

#### CONDITIONS.

C.D. . . . .	3 to 6 amperes.
E.M.F. . . . .	5 to 7 volts.
Temp. . . . .	should not rise above 20°

According to the equation, 15 gm. of caffeine requires the passage of 8.4 ampere hours of current.



It is better to give it slightly more than this in order to ensure complete reduction, say 10 ampere hours.

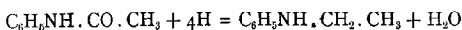
As soon as the reduction is complete, the cathode fluid is diluted with an equal volume of water, and neutralised with slaked

<sup>1</sup> T. B. Baillie and J. Tafel, *Ber.*, **32**, 68.

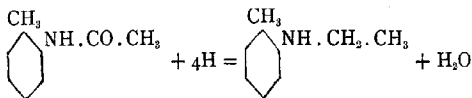
lime, the precipitated calcium sulphate filtered off and washed once with water. The wash water is added to the original solution, and the whole evaporated to 60 or 70 c.c. on the water bath. The concentrated solution is now extracted several times with chloroform; the chloroform is then distilled off, when there remains a yellowish crystalline residue. This crystalline residue is dissolved in a small quantity of 10-per-cent. hydrochloric acid, and the solution shaken out with chloroform; this dissolves out the colouring matter, and any unchanged caffeine which may have escaped reduction. The solution is now made alkaline with caustic alkali, and again extracted several times with chloroform. On evaporating the chloroform the desoxycaffeine is obtained in a very pure condition, in the form of colourless crystals. It can be further purified by crystallisation from ethyl acetate. The desoxycaffeine so obtained contains 1 mol of water of crystallisation  $C_8H_{12}N_2O_5 \cdot H_2O$ ; m.p.  $118^\circ$ . When dried over sulphuric acid *in vacuo* the water of crystallisation is given up, and the m.p. rises to  $148^\circ$ . The water-free substance can be distilled undecomposed *in vacuo*. The yield of the pure product is about 70 per cent.

### XXXV. Preparation of Ethyl-o-toluidine.<sup>1</sup>

Another interesting case of reduction of the carbonyl group is the reduction of the acetanilides as, for example, acetanilide, which is converted into ethylaniline.



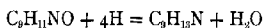
The acet-toluidines yield ethyl toluidines, thus orthotoluidine gives ethyl-o-toluidine.



Dissolve 10 grm. of acetyl-o-toluidine in a mixture of 35 c.c. concentrated sulphuric acid and 45 c.c. of water. This is then

<sup>1</sup> T. B. Baillie and J. Tafel, *Ber.*, **32**, 68.

electrolysed in a porous cell as cathode space, with a prepared lead electrode. The porous cell is placed in a lead vessel, which acts as anode, and is filled with 20-per-cent. sulphuric acid. If preferred, the cell can be placed in a beaker, and a cylinder of lead be employed as anode. The whole apparatus is placed in cold water, otherwise considerable heating takes place. A current of about 5 amperes is passed; the current density is not of great importance, provided the temperature does not rise too high—it should not be allowed to rise above 25°.



10 grm. of acet-toluide requires just over 7 ampere hours for complete reduction; about 8.5 ampere hours of current is passed and the electrolysis stopped.

The cathode solution is diluted with about  $1\frac{1}{2}$  times its volume of water, and allowed to stand overnight. Some unchanged acet-toluide crystallises out; this is filtered off, and the filtrate rendered alkaline with caustic alkali, and steam-distilled. In order to purify the product, the distillate is made acid, and sodium nitrite added a little at a time, the mixture at the same time being cooled, to convert the ethyl toluidine into the nitrosamine. The oily nitrosamine is then separated from the solution, and reduced with tin and hydrochloric acid, by which means it is reconverted into the ethyl-o-toluidine, which after making the solution alkaline is extracted with ether. The boiling-point of the ethyl-o-toluidine is 213° to 214°. Yield, about 60 per cent. of the theory.

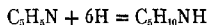
### XXXVI. Preparation of Piperidine (Hexahydropyridine).

Dissolve 20 grm. pyridine in 200 c.c. of 10-per-cent. sulphuric acid. Place this solution in a glass electrolysing cell with a lead cathode, and a rather smaller anode also of lead. As neither pyridine nor piperidine are oxidised to any extent by the anode current, it is not necessary to separate the anode and cathode.

## CONDITIONS.

C.D. . . . .	10 to 12 amperes.
E.M.F. . . . .	6 to 8 volts.
Temp. . . . .	Normal; rises during electrolysis to 50° or 60°

When the circuit is first closed there is scarcely any hydrogen gas given off at the cathode, almost the whole of it being used up to reduce the pyridine to piperidine.



But as the electrolysis is continued more and more, gas is given off at the cathode until finally the evolution of gas is quite vigorous. When rather more than the theoretical amount of current has been passed, it is switched off. The solution is then rendered alkaline with caustic soda, and steam-distilled. The piperidine passes over with the steam, which should be vigorously driven into the solution, and the distilling flask should also be heated on a sand bath. The strongly alkaline distillate, which possesses the peculiar and characteristic odour of piperidine, is acidified with hydrochloric acid and evaporated to dryness. The solid piperidine hydrochloric is then decomposed with a strong solution of caustic potash. If the mixture does not separate into two layers, a few small pieces of solid caustic potash are added. The upper layer consisting of piperidine is then separated, dried with solid caustic potash and fractionated. The boiling-point of piperidine is 106°.

## LITERATURE

Ahrens, *Zeit. f. Elektrochem.*, **2**, 577. Merck, *D.R.P.*, 1896, 90308.

## CHAPTER XV.

### *OXIDATION OF ORGANIC COMPOUNDS.*

THE number of compounds which have been successfully prepared by electrolytic oxidation is comparatively small. The chief difficulty in oxidising is to stop the reaction at the right point. One might suppose this to be a comparatively easy matter, it being only necessary to pass the current sufficiently long to liberate a given amount of oxygen, and that then the oxidation should be complete. For example, if one atom of oxygen is required to oxidise a certain substance, then, if 2 faradays or  $96,540 \times 2$  coulombs of electricity is passed, the oxidation will have taken place. But here, as with all oxidations, the reaction often proceeds too far: a portion of the substance only may have been attacked, and attacked much too vigorously—in other words, burnt up; whereas a portion will have been altogether unacted upon. To exactly state what are the conditions necessary for successful electrical oxidation is an impossibility; generally speaking, it seems important to keep the E.M.F. as low as possible: other conditions, hot or cold, acid or alkaline solutions, and so forth, will vary with the substance to be oxidised.

### **XXXVII. Preparation of Purpurogallin.**



Dissolve 28 grm. (1 oz.) pyrogallol in 500 c.c. of a 15-per-cent. solution of sodium sulphate. Place this solution in a rectangular glass jar, which should stand in a basin of cold water.



At the two opposite corners of the jar fix two thin pieces of composition pipe, to each of which a piece of copper wire has been soldered. Connect these wires together, and join them up with the negative pole of the electrical supply. The anode must be of platinum, and it is best to have it rotating. If a rotating platinum anode is not to be had, then hang two pieces of platinum foil at opposite sides of the jar, and vigorously agitate the solution by means of a glass or wooden stirrer. The anode surface should not be less than 1 square decimeter, but is better to have double that surface.

## CONDITIONS.

C.D. . . . .	1·5 to 2 amperes.
E.M.F. . . . .	4·3 to 4·5 volts.
Temp. . . . .	Normal.

With a current of 2 amperes the electrolysis is completed in 6 to 8 hours. As soon as the current is switched on, the solution becomes yellow, and in a short time a yellow or orange yellow precipitate of purpurogallin begins to separate out. The solution should not be allowed to become hot, otherwise a brown impure product is obtained; it is therefore advisable to stand the electrolysing cell in a basin of cold water. After the electrolysis is finished, allow the product to stand overnight, then filter and wash with water; finally spread on a porous plate to dry. The purpurogallin so obtained is of a bright yellow colour, and is quite pure.

Yield about 10 grm. It can be crystallised from hot glacial acetic acid, from which it separates, on cooling, in dark yellow needles or plates. If a very small quantity of purpurogallin is shaken up with water containing a drop or two of ammonia or caustic alkali, a magnificent blue colour is produced, which gradually becomes brown; this reaction only shows in dilute solutions. Purpurogallin has well-marked tinctorial properties, giving with mordants much the same shades as alizarine. The interesting point about purpurogallin is, that in it we have a benzene derivative passing by simple oxidation into a derivative

of naphthaline. The exact constitutional formula of purpurogallin is not at present known.

## LITERATURE.

A. G. Perkin, *Chem. Soc.* (1903), **83**, 192; A. G. Perkin and F. M. Perkin, *Chem. Soc.* (1904), **85**, 243.

## XXXVIII. Preparation of Iodoform.



## From Alcohol.

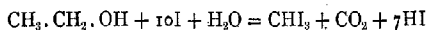
Dissolve 20 grm. dry sodium carbonate and 20 grm. potassium iodide in 200 c.c. water, then add 50 c.c. of absolute alcohol. Methylated spirit which has been purified by distillation over caustic soda and lime may be used instead of the absolute alcohol.

**Anode.**—Sheet platinum.

**Cathode.**—Platinum or nickel; it should be in the form of a spiral of stout wire, and the surface should be considerably less than the anode surface.

Heat the solution to a temperature of  $60^\circ$  to  $70^\circ$ , and then electrolyse with an anode current density of 1 to 3 amperes. The beaker employed should be a high one, so that the upper surface may help to condense the alcohol, which is otherwise apt to volatilise. During the electrolysis a slow stream of carbonic acid gas should be conducted through the mixture in order to prevent the solution becoming too alkaline, owing to the liberation of sodium at the cathode. It is also advantageous to agitate the solution vigorously by means of a mechanical stirrer—a rotating platinum anode serves this purpose very well. If during the electrolysis the solution should become brown, owing to liberation of iodine, the passage of the carbonic acid gas must be stopped until the brown colour disappears, because the appearance of the brown coloration shows that the carbonic acid gas is being passed too rapidly.

The reaction which takes place is represented by the following equation :—



The hydrogen iodide produced recombines with the liberated sodium and potassium at the cathode to reform potassium iodide. The iodine shown in the above equation is, of course, obtained from the electrolysis of the potassium iodide.

The electrolysis may be allowed to continue for three hours, at the end of which time the current is cut off and the solution allowed to stand for two or three hours, or better over night, when the iodoform is filtered off. The iodoform so obtained is in the form of small crystals, and is very pure. The current efficiency is between 75 and 80 per cent.

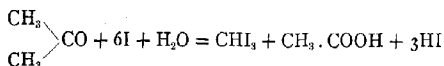
The solution which is left over may again be employed by adding a fresh quantity of alcohol and potassium iodide, so that the process can be made practically continuous; this is, of course, important when the operation is conducted on a manufacturing scale.

During the electrolysis, a certain portion of the iodide becomes oxidised to iodate. A certain amount of reduction of the iodoform always takes place at the cathode, so Elbs suggests surrounding the cathode with parchment paper; but when large quantities of iodoform are required, it is better to employ a porous cell for the cathode department. In a continuous process, the anode solution may be changed to the cathode after each filtration, as the iodate thus becomes reduced to iodide again, and is then ready to be again placed in the anode compartment. The disadvantage in using a porous cell is that the E.M.F. is slightly raised.

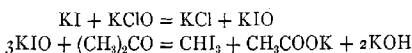
#### **With Acetone.**

In the equation already given for the production of iodoform from alcohol and iodine, it is seen that for every molecule of iodoform produced, 10 atoms of iodine is required. With acetone,

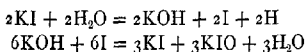
on the other hand, only 6 atoms of iodine is required to produce one molecule of iodoform.



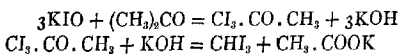
When alcohol is oxidised, 1 ampere hour will theoretically yield 1.467 grm. of iodoform; but with acetone, 1 ampere hour gives 2.444 grm. It follows, therefore, that if acetone can be substituted for alcohol, there would be a great saving in the current required: furthermore, acetone is cheaper than alcohol. When a mixture of potassium iodide, sodium carbonate, and acetone is electrolysed under the same conditions as those set out above for the preparation of iodoform from alcohol, only very small quantities of iodoform are produced. But it has recently been shown by Abbot that fairly good results can be obtained by allowing the acetone to run in very slowly during the course of the electrolysis. The following method, due to T. E. Teeple, gives extremely good results, the yields often being up to 95 per cent. of the theoretical. In the commercial chemical process for manufacturing iodoform from acetone, according to the method of Suilliot and Raynand, the production of the iodoform depends upon the formation of potassium hypoiodite by the action of a hypochlorite upon potassium iodide.



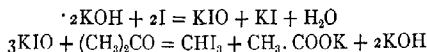
If now a solution of potassium iodide is electrolysed at ordinary temperatures, potassium hypoiodide is produced.



If acetone is also present, it will react with the hypoiodide in the following manner:—



In order to obtain a good yield of iodoform, it is necessary to neutralise the excess of caustic potash formed in the reaction; this may either be done by passing in carbonic acid gas, neutralising with hydrochloric acid, or, better still, with iodine.



It will be seen that caustic potash is again set free by the further electrolysis, and we therefore obtain a continually decreasing quantity,  $\frac{1}{3} + \frac{1}{9} + \frac{1}{27} + \dots = \frac{1}{2}$ . It follows, therefore, that the necessary quantity of iodine to add is exactly half as much as the quantity which the electric current liberates.

**Process.**—Dissolve 25 gm. of potassium iodide in 225 to 250 c.c. water, add 3 c.c. of acetone, and electrolyse with a platinum cathode—a spiral of stout wire—and a platinum anode of from  $\frac{1}{2}$  to 1 square decimeter. It is best to employ a rotating anode, or to thoroughly agitate the solution by means of a glass stirrer.

#### CONDITIONS.

C.D. . . . .	1'5 to 1'75 ampere.
E.M.F. . . . .	3'5 to 3'75 volts.
Temp. . . . .	Normal.

The electrolysis may be conducted for about 90 minutes, during which time 1'56 gm. of iodine is added in small quantities at a time, sufficiently quickly to keep the solution just brown in colour. After the electrolysis has proceeded for about 45 minutes, another 3 c.c. of acetone may be added.<sup>1</sup> At the end of 90 minutes or so the electrolysis is stopped, and the mixture allowed to stand for about an hour and a half. After which the iodoform is filtered off and washed with a little water. If it is brown in colour it should be also washed with small quantities of a dilute solution of sodium carbonate. Yield of iodoform, 92 to 94 per cent.

Instead of adding iodine, a fairly rapid stream of carbonic acid gas may be conducted through the electrolyte during the

<sup>1</sup> Teeple only recommends the addition of 2 c.c. of acetone altogether; the author has, however, obtained better results by proceeding as above.

first fifty minutes of the electrolysis, after which it is discontinued. The solution will probably be very brown in colour, and the colour may not have completely disappeared when the current is stopped. In about an hour's time after the current has been cut off, the brown colour will probably have completely vanished.

The iodoform is obtained in the form of a fine crystalline powder. It can be obtained in large crystalline plates by crystallizing from acetone. But the colour of the product keeps better when the iodoform is crystallised from alcohol.

#### LITERATURE.

Elbs und Herz, *Zeit. f. Elektrochem.*, **4**, 113; A. Foerster and Meves, *Zeit. f. Elektrochem.*, **4**, 268; Schering, *D.R.P.*, 29771; Howe Abbot, *Journ. Physical Chem.*, **1903**, 84. Teeple, *Journ. Amer. Chem. Soc.* (1904), XXVI. 170.

### XXXIX. Preparation of Bromoform.<sup>1</sup>

Sixty grams of potassium bromide and 0.3 gm. of potassium chromate is dissolved in 150 c.c. of water, and to the solution is added 20 c.c. of acetone. This solution is then placed in a beaker capable of holding about 200 c.c.

The anode should be of sheet platinum, bent cylindrically, so that when placed in the beaker it fits almost against the walls of the vessel. The active anode surface may be about 50 sq. cm.—practically only the inner surface of the anode, when arranged as here described, will be active. The cathode, which is a spiral of stout platinum wire capable of carrying 4 or 5 amperes without becoming hot, is placed in the centre of the beaker, so that it is surrounded by the cylindrical anode. A cylinder, such as is used for electro-analytical purposes, serves very well as anode.

In order that the temperature may not rise above 18° to 20° the beaker is placed in a basin through which cold water is caused to circulate during the experiment. A current of about 3 amperes

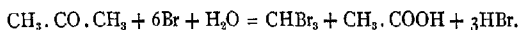
<sup>1</sup> E. Muller and R. Loebe, *Zeit. f. Elektrochem.*, 1904, **X**, 409.

is passed; the E.M.F. will be about 4 to 4.2 volts. During the electrolysis a rapid stream of carbonic acid gas is conducted through the solution. The tube from which the carbonic acid gas is delivered should pass to the bottom of the beaker, so that the bromoform, as it is formed, may, as well as the solution, be agitated. In order to obtain a thorough agitation, the delivery tube may consist of a T tube bent twice at right angles, the ends of the tube being drawn out into narrow openings.

After the passage of about 14 ampere hours the current is stopped, when the bromoform, strongly coloured with bromine, settles to the bottom of the beaker. The mixture is transferred to a separating funnel, and separated from the electrolyte. It is then shaken up in the separating funnel with a mixture of acetone, and sodium carbonate solution. This solution is added in small quantities at a time, the addition being continued until the brown colour disappears. The brown coloration due to the bromine varies very much in intensity in different experiments; sometimes the bromoform is coloured a deep red, at other times it is only light brown. The cathode should not be nickel, because the liberated bromine acts upon it, and the yield of bromoform is very much less than when the cathode is of platinum. There seems also a tendency with a nickel cathode for bromo-acetones to be produced, and these are extremely irritating to the eyes.

The bromoform is finally washed with a little water, and its volume measured, the weight being obtained by multiplying the number of cubic centimeters obtained by 2.9, the sp. gr. of bromoform. So obtained, the bromoform always contains a trace of moisture, which causes it to be cloudy. In order to render it anhydrous, the bromoform must be dried over calcium chloride, and distilled; the b.p. is  $151^{\circ}$ , and the m.p.  $7.6^{\circ}$ .

The reaction which takes place in the formation of bromoform may be represented by the equation—



In the electrolytic production of bromoform from potassium bromide and acetone, potassium hydroxide is produced, and it

is to render this innocuous that carbonic acid gas is passed through the electrolyte. The addition of the potassium chromate is to prevent, as far as possible, the reducing action of the hydrogen; the employment of a high cathode density also helps in this direction.

## XL. Preparation of Anthraquinone.



The electrolytic oxidation of anthracene is attended with certain difficulties, because anthracene is a solid substance which is only very difficultly soluble in organic reagents: the only one which can be employed is acetone, but with this solution it is not possible to obtain very satisfactory yields of anthraquinone. Recourse is therefore had to oxidation of an emulsion of the solid anthracene which has been ground to a very fine powder.

Anthracene is a substance which it is very difficult to wet satisfactorily, but unless it is thoroughly wetted a good emulsion cannot be formed. By dissolving it in acetone or in acetic acid, and pouring into water, a good mixture can be obtained. Perhaps, however, the best method to adopt is to rub the finely powdered anthracene through a wire gauze of very fine mesh with warm water; this is a somewhat tiresome procedure, but it gives very satisfactory results.

If a mixture of anthracene in sulphuric acid or in caustic alkali is subjected to the oxidising action of the electric current, only a very small amount of oxidation takes place. It is found, however, that if an oxygen-carrier is added to the mixture, over 80 per cent. of the anthracene can be oxidised to anthraquinone. Various oxygen-carriers have been suggested, such as manganese chromium or cerium salts, all of which give satisfactory results.

**Procedure.**—A circular lead vessel is made the anode; it should have a capacity of about 1500 c.c. of solution. The cathode, which should be capable of very vigorous rotation, is also of lead,



e.g. a lead paddle (p. 198) ; the entire cathode surface should not exceed half a square decimeter.

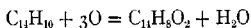
Mix 20 grm. of anthracine with water in the manner just described, and wash it into the anode vessel ; dilute to 900 c.c., and add 100 c.c. concentrated sulphuric acid. The oxygen-carrier is now added, and may be 150 grm. chrome alum, 20 grm. potassium chromate, 100 grm. manganese sulphate, or 1.5 grm. ceric sulphate. The total exposed anode surface will be from 5 to 6 square decimeters.

#### CONDITIONS.

C.D. . . . .	1 to 2 amperes.
E.M.F. . . . .	2.8 to 3.5 volts.
Temp. . . . .	75° to 90°

The cathode must be very rapidly rotated in order that the anthracine may be thoroughly incorporated with the solution.

When an oxygen-carrier is used, there seems very little advantage in employing a porous cell to separate the anode and cathode, so long as the anode surface is very large in comparison to the cathode. From the equation it will be seen that every gram of anthracine requires about 1 ampere hour to oxidise it to anthraquinone.



After the current has been passed for about 22 ampere hours, the electrolysis is stopped. Towards the end of the reaction it is advisable to cut the current down to about  $\frac{1}{2}$  ampere per square decimeter, and to raise the temperature to 100°. When a cerium salt is used as oxygen-carrier, the end of the operation is known by the solution retaining a permanent yellow colour, due to unreduced ceric sulphate.

When cool the mixture is filtered and the anthraquinone washed with water until the filtrate is no longer acid. It is then spread on a porous plate, and when dry may be crystallised from toluene or benzene or a mixture of acetone and toluene. Since there is still from 10 to 12 per cent. of anthracine present, the mother liquor should be poured off from the anthraquinone, which

separates out first, before it is quite cold. One crystallisation, if this precaution is taken, is generally sufficient to give a perfectly pure product. The anthraquinone is obtained in the form of beautiful light yellow silky needles; m.p.  $274^{\circ}$ .

It is a rather interesting point, that, although without a diaphragm (even when a small cathode and large anode surface is employed), it is only possible to oxidise a comparatively small quantity of chromic salt to a chromate. Yet in spite of this it makes a very satisfactory oxygen-carrier for oxidising organic substances such as anthracene. It is quite likely that the lead peroxide produced at the anode may also take part in the oxidation. In fact, one very rarely notices any deposit of lead peroxide on the anode vessel when the reaction is finished.

#### LITERATURE.

Darmstadter (1897), *D.R.P.*, 109,012; Höchst Farben Fabrik, *D.R.P.* (1898, 103,860); Le Blanc, *Zeit. f. Elektrochem.* (1900), 7, 292; and *Darstellung des Chroms.*, A. Fontana and F. M. Perkin, *Electrochemist* (1904), III, 656.

## PREPARATION OF DYES.

### XLI. Preparation of Canarine.<sup>1</sup>



When potassium or ammonium thiocyanate is electrolytically oxidised in presence of hydrochloric acid, a yellow precipitate called canarine is produced, the constitution of which has not yet been determined, but which has had the formula  $\text{C}_9\text{H}_7\text{HS}_2$  assigned to it. This substance, which is insoluble in acids and in the ordinary organic solvents, dissolves in alkali carbonates and hydroxides and in borax solution. Silk and wool, when immersed

<sup>1</sup> Prochoroff und Müller, *Dingler's Journal*, **253**, 130; Markognikoff, *Journ. Russian Chem. Soc.*, **1884**, 380; Lindow, *Ibid.*, **1884**, 271; references in *Ber.*, **17**, R. 279 and 522; and *Ber.*, **18**, R. 676.

in solutions of canarine, are dyed a yellow, the intensity of the colour depending upon the amount of canarine in the solution. When cotton goods are impregnated with this dye, it acts as a mordant toward basic colouring matters.

**Preparation.**—Dissolve 30 grm. ammonium or potassium thiocyanate in about 300 to 400 c.c. of distilled water. Transfer this solution to a narrow beaker, fitted with a cork through which passes a glass stirrer (Fig 62). On either side of the glass stirrer is hung an electrode of sheet platinum, about  $\frac{1}{2}$  square decimeter

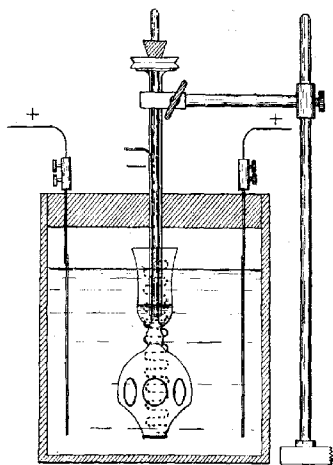


FIG. 62.

in surface, and on the other two sides spirals of platinum wire, one of which is shown in the diagram (diameter about 0.75 to 1 mm.). The two larger electrodes act as anodes and the smaller electrodes as cathodes. Before commencing the electrolysis, the solution is heated to 75° or 80°, and then 20 c.c. of strong hydrochloric acid run in by means of a thistle funnel, which passes through a hole in the cork; the current is then switched on.

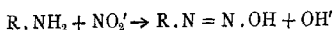
## CONDITIONS.

C.D. . . . .	5 to 6 amperes.
E.M.F. . . . .	3.0 to 3.5 volts.
Temp. . . . .	80°

The best form of glass stirrer to use is that described by W. Löb;<sup>1</sup> this form of stirrer is exceedingly efficient, and never wobbles.<sup>2</sup> Fig. 62 shows the arrangement of the cell. If the cell is not kept enclosed during the course of the electrolysis, the vapours which come off are extremely unpleasant and poisonous, and produce headache. A tube, not shown in the diagram, passes through the cork, so that the gas evolved can be led off or collected, as may be desired. Shortly after the electrolysis has commenced, a light yellow precipitate commences to fall out, and the mixture assumes a uniform yellow tint. After the current has been passed for about four hours, the electrolysis is stopped. The mixture is allowed to stand until cold, and then filtered off. The canary yellow precipitate is washed several times with warm water, and then spread upon a porous plate, in order to remove the last traces of moisture. Yield about 5 grm.

## Azo-Compounds.

W. Löb<sup>3</sup> finds that, when an amine, a nitrite, and a coupling substance, such as a phenol, are mixed together, and subjected to electrolysis in the anode compartment, azo-colouring matters are produced. It must be presumed that a diazo-compound is first formed by the action of the  $\text{NO}_2$  ions at the moment of their liberation, for which we may write the equation—



The main difficulty in the reaction is the unstable character of the diazo-compound under the influence of the electric current. It is therefore necessary to have the coupling agent present from the

<sup>1</sup> *Zeit. f. Elektrochem.*, **7**, 117 (1900).

<sup>2</sup> When it is desired to keep the electrolytic cell absolutely gas-tight, then the vessel A is partially filled with mercury, as shown in the figure.

<sup>3</sup> *Zeit. f. Elektrochem.*, 1904, **X**, 237; *D.R.P.*, 761, 310, 1904.

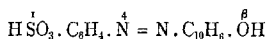
very commencement, so that the azo-compound is formed. By this means it is precipitated, or, if not precipitated, converted into the more stable substance, and thus removed from the further action of the electric current.

An amine cannot be employed as coupling or fixing agent, because the amine itself will react with the discharged  $\text{NO}_2^+$  ions. Löb finds, however, that phenols may be very satisfactorily employed. The sodium nitrite, amine, and a phenol are mixed together, and electrolysed in the anode compartment with a platinum electrode. It is necessary to vigorously agitate the solution.

## XLII. Preparation of Orange II.

(Tropäolin 000 No. I.)

$\beta$ . Naphthol-azobenzenemonosulphonate.



Add 19.5 grm. of the sodium salt of sulphanilic acid (p-amido-benzene sulphonic acid), 14.4 grm. of  $\beta$ . naphthol, and 6.9 grm. sodium nitrite<sup>1</sup> to 150 c.c. of water. Place this mixture in the anode compartment, which may consist of a beaker or a rectangular battery jar.

The cathode compartment should consist of two small porous cells, of such a size that either a platinum or glass stirrer can be rotated between them. The cathode solution may consist of 10-per-cent. caustic soda.

The cathode should be either nickel or platinum wire—the anode either a stirrer of platinum or a sheet of platinum; in the latter case a glass stirrer (Fig. 62, p. 272) must be employed, because, as the substances used are not all soluble in water, it is essential to have a very thorough agitation of the mixture. The whole apparatus is placed in a basin through which cold water is

<sup>1</sup> It is necessary to first test the quality of the sodium nitrite, because the ordinary product is rarely pure. The above numbers refer to the 100-per-cent. product.

passed—it is, in fact, an advantage to surround the electrolysing apparatus with ice.

If the anode mixture is placed in a porous cell, the outer cell acting as cathode, there is considerable difficulty in keeping the temperature of the mixture sufficiently low. When larger quantities than the above are prepared, the apparatus depicted in Fig. 63 may be employed.

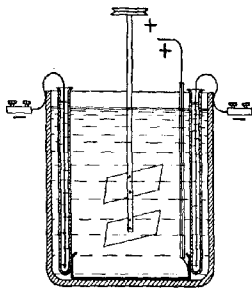


Fig. 63.

The apparatus consists of a rectangular battery jar, on either side of which is placed a porous cell, containing the cathode solution. The anode consists of a platinum rotator, and, in order to increase the anode surface, a sheet of platinum is fixed at the bottom of the vessel, as shown in the figure. Or two sheets of platinum may be hung about 1 c.m. from each side of the cathode cells, and a glass stirrer can be employed. The whole apparatus is placed in a vessel of cold water, to which ice is added in order to maintain as low a temperature as possible.

#### CONDITIONS.

C.D. . . . .	8 to 12 amperes.
E.M.F. . . . .	18 to 15 volts.

As the sodium nitrite gets used up in the reaction, the E.M.F. is inclined to rise. Therefore Löb recommends the employment of sodium nitrate as the cathode solution; the only drawback to this is that, as the electrolysis proceeds, the anode solution gets acid from the migration of the  $\text{NO}_3$  ions. This can be prevented by occasional addition of small quantities of dilute caustic soda.

In order to complete the reaction, about twice the theoretical amount of current should be passed.

If during the electrolysis frothing takes place, it can be prevented by adding a few cubic centimeters of dilute caustic soda.

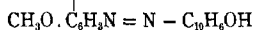
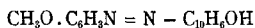
When the electrolysis is carried out at a temperature of  $0^{\circ}$  a considerable quantity of the colouring matter crystallises out, which can be filtered off; it usually contains, however, small amounts of  $\beta$ . naphthol, for this reason it is advisable to add sufficient water to dissolve all the orange II. and filter from the unchanged  $\beta$ . naphthol. Excess of alkali must not be present, otherwise the  $\beta$ . naphthol will also dissolve.

The colouring matter can be obtained from this solution by evaporating to dryness on the water bath and extracting with alcohol. On evaporating off the alcohol the orange is obtained as a dark yellow powder. Or the colouring matter may be precipitated in the form of its insoluble barium salt by the addition of barium chloride. The barium salt forms a yellow powdery precipitate, which can be filtered off and washed with water. Again, the colouring matter may be salted out by addition of excess of sodium chloride.

On a technical scale the colouring matter can be estimated by making direct quantitative dyeing experiments with the anode solution. Orange II. dyes wool and silk a brilliant yellow.

By using  $\alpha$ . naphthol as coupling substance instead of  $\beta$ . naphthol, Orange I. or Tropäolin 000 No. II. is produced.

### XLIII. Preparation of Dianisidine Blue.<sup>1</sup>



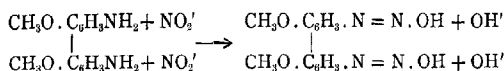
24.4 grm. dianisidine, 28.8 grm.  $\beta$ . naphthol and 13.8 grm. of sodium nitrite are mixed with 250 c.c. water, and placed in the anode cell, and treated in exactly the same manner as that described in the preceding preparation, the C.D. and all the other particulars being similar.

During the electrolysis the dianisidine blue precipitates completely out. It is purified by dissolving it in caustic alkali,

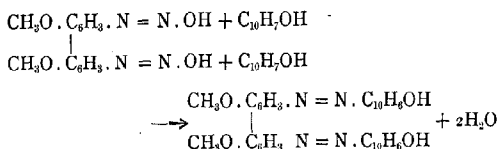
<sup>1</sup> The particulars of the electrolytic preparation of azo-colouring matters were kindly communicated to me by Dr. Löb, to whom my thanks are due.

precipitating with dilute sulphuric or hydrochloric acid, and washing with water.

The reaction may be expressed by the following equation, in which the action of the  $\text{NO}_2'$  anions is represented as producing the diazo-compound upon acting upon the dianisidine (dimethoxybenzidine).



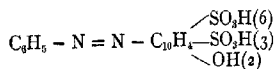
The diazodianisidine in presence of  $\beta$ , naphthol couples up with this, and forms the dianisidine blue.



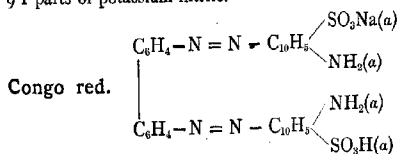
A similar reaction applies in the case of the preparation of orange II.

Other azo-colouring matters can be prepared in a similar manner.<sup>1</sup> For example,—

**Ponceau 2. G**, benzene-azo-2-naphthol-3 : 6 disulphonic acid.



The anode bath in this case consists of 10 parts by weight of aniline, 32.7 parts of  $\beta$ , naphthol disulphonic acid (R. acid), and 9.1 parts of potassium nitrite.



<sup>1</sup> *D.R.P.*, 761,310, 1904.



This substance can be prepared by electrolysis, in the anode compartment, 10 parts of benzidine, 33 parts of the sodium salt of naphthionic acid (1, 4 Naphtylamine sulphonic acid), and 9.3 parts potassium nitrite. The bath being kept at a temperature of 60° to 90°. During the electrolysis the bath should not be allowed to become acid, therefore the cathode solution should consist of 10-15 per cent. caustic soda.

## OXIDATION OF BENZENE DERIVATIVES.

When toluene, the xylenes, or the mesitylenes are oxidised with platinum electrodes—to a less extent with peroxidised lead electrodes—the methyl group, or one of the methyl groups, is oxidised to the aldehyde group. This oxidation to aldehyde, *i.e.* the second stage of oxidation, is unusual, most oxidising agents carrying the oxidation a stage further to produce the carboxyl group. The influence of the position of the methyl groups to each other is also of interest, for whereas with toluene, generally speaking, the yield of benzaldehyde is not more than 13 to 14 per cent., with ortho- and para-xylene between 30 and 35 per cent. of the corresponding mono-aldehydes can be obtained. With meta-xylene, however, the yield is very poor, rarely exceeding 10 or 15 per cent., and it may often be less.

The influence of a negative group is also very striking; it is a well-known fact that ordinary oxidising agents have very little action upon the methyl group in the cresols, the negative hydroxyl exerting a protective action. With electrolytic oxidation a similar difficulty is met. The electrolytic oxidation of the nitrotoluenes is also of interest when these substances are oxidised under similar conditions to those which yield benzaldehyde or the toluene aldehydes, only a very small quantity of the nitroaldehyde is produced, the bulk of the substance being unacted upon. Elbs<sup>1</sup> and Pierron<sup>2</sup> have found that when para- and ortho-nitrotoluene are dissolved in acetic acid and subjected to electrolytic oxidation,

<sup>1</sup> *Zeit. f. Elektrochem.*, **2**, 522.

<sup>2</sup> *Bull. Soc. Chem.*, **25**, 852.

the chief product is the corresponding nitrobenzyl alcohol. Pierron, *loc. cit.*, has further found that with meta-nitrotoluene the aldehyde is produced.

#### XLIV. Preparation of Benzaldehyde.

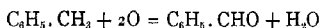
For the preparation of benzaldehyde an apparatus with a stirrer, similar to that employed for the preparation of canarine (p. 272, Fig. 62), should be used. When this apparatus is employed, it is not necessary to use a diaphragm or porous cell to separate the anode from the cathode, because the anodes are so much larger than the cathode. Under these circumstances the cathodic hydrogen exerts very little reducing action. The anode surface should be from 1 to 2 square decimeters in area; the cathode, about 2 to 4 square centimeters.

**Process.**—Weigh out 50 gm. of toluene into the electrolyzing cell, and add 200 c.c. of 10-per-cent. sulphuric acid and 250 to 300 c.c. of acetone. Stand the cell in a basin through which cold water can be circulated, and connect up the electrodes.

##### CONDITIONS.

C.D.	1.5 to 2 amperes.
E.M.F.	5 to 6 volts.
Temp.	Not above 20°

The stirring must be sufficiently vigorous to keep the mixture in a thorough emulsion. From the equation it is seen that



5 gm. of toluene requires the passage of about 58 ampere hours. In order to make sure that the toluene is all oxidised, about 65 ampere hours of current should be passed, but a large excess of current is not advisable.

When the electrolysis is finished, the mixture is transferred to a flask, the excess of acid neutralised with sodium carbonate (the solution must not be made strongly alkaline), and the acetone distilled off. The residue is then steam-distilled, when

the benzaldehyde and any unchanged toluene passes over, a considerable quantity of a resinous substance remaining behind in the flask. In order to purify the benzaldehyde, and separate it from unchanged toluene, the distillate is extracted with ether and shaken up with sodium hydrogen sulphite. After allowing to stand overnight, the bisulphite compound is filtered off, washed with alcohol and ether, and placed in a flask. A little dilute caustic soda solution is added, after which it is steam-distilled. On extracting the distillate with ether, drying over calcium chloride, and distilling off the ether, the benzaldehyde is obtained in the pure condition. Yield, 7 to 8 grm.

The ethereal solution obtained when the bisulphite compound is filtered off, contains a small quantity of a neutral substance which may either be benzyl alcohol or a condensation product of partially oxidised toluene.

The oxidation of ortho- or para-xylene gives very good results; but owing to the expense of these substances, the oxidation of toluene has been given. The method of procedure with the xylenes is exactly the same as with toluene.

#### LITERATURE.

Benard, *Compt. Rendus*, **91**, 175; Merzbacher and Smith, *Amer. Chem. Soc.*, **22**, 723; K. Puls, *Chem. Zeitung*, **25**, 263; H. D. Law and F. M. Perkin, *Trans. Faraday Society*, **1904**, 31.

### XLV. Preparation of Para-nitrobenzyl Alcohol.

A porous cell is used as anode compartment, and in this is placed an anode of sheet platinum or of platinum gauze. The anode solution consists of 80 c.c. glacial acetic acid, 8 c.c. concentrated sulphuric acid, and 15 grm. of para-nitrotoluene.

The porous cell is placed in a beaker and surrounded with a cylindrical cathode of sheet lead, the electrolyte being sulphuric acid, 1.6 to 1.7 sp. gr. The whole apparatus must stand in a water bath, which is kept at boiling temperature during the electrolysis.

## CONDITIONS.

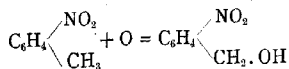
C.D. . . . .	1 to 1.5 ampere.
E.M.F. . . . .	4 to 4.5 volts.

It will be noticed that during the electrolysis very little hydrogen is evolved at the cathode, because it is mainly required to reduce the strong sulphuric acid which forms the electrolyte, and, as a consequence, sulphur separates out. Three times as much current must be passed into the mixture as is theoretically required.

At the end of the operation the mixture is steam-distilled, by which means unchanged para-nitrotoluene is driven over; a small portion of the p-nitrobenzyl alcohol also passes over. The oily content of the flask is now filtered, while still hot, through a wet double filter paper; by this means the main portion of a resinous material remains behind; this is then twice washed with hot water and the washings added to the filtrate.

On cooling, crude p-nitrobenzyl alcohol crystallises out in long dirty yellow needles; these are filtered off, and the mother liquor shaken out with ether. The ethereal solution contains a mixture of p-nitrobenzyl alcohol and p-nitrobenzyl acetic ester ( $\text{CH}_3 \cdot \text{CO} \cdot \text{OCH}_2 \cdot \text{C}_6\text{H}_4\text{NO}_2$ ). The ether is distilled off, and the residue extracted with small quantities of alcohol. The alcoholic extract contains only the p-nitrobenzyl alcohol.

The crystals and the product from the alcohol are then mixed together and purified by boiling with water and animal charcoal; on filtration the pure product crystallises out. Yield, 35 to 40 per cent.



## Preparation of Some of the Reagents and Materials.

**Solution of Sodium Monosulphide,  $\text{Na}_2\text{S}$ .**—Dissolve sufficient sodium hydroxide—purified from alcohol—in water, to form a solution of sp. gr. 1.24 to 1.26. Saturate the solution with sulphuretted hydrogen. In spite of the sodium hydroxide being purified, there is generally more or less precipitate produced; filter this off. Now evaporate the solution down in a porcelain basin placed on a sand bath, until about one quarter of it has evaporated away. The solution should be poured into bottles while still hot, and the bottles closed with rubber stoppers. Glass stoppers are liable to become fixed and immovable.

**Ammonium Borate and Ammonia.**—Dissolve 35 gm. of ammonium borate in 700 c.c. of water—it may be necessary to warm the mixture; and when cool add 300 c.c. of ammonium hydrate, sp. gr. 0.88. This solution is used in the analysis of nickel and cobalt (pp. 95 and 98).

**Cobalt Ammonium Sulphate.**—Dissolve equi-molecular proportions of cobalt and of ammonium sulphate in separate quantities of hot water; the solutions should be made nearly saturated. Mix the two solutions while still hot, and place in a beaker surrounded with cold water. While the solution is cooling, it should be vigorously stirred with a glass rod. The cobalt double salt separates out in the form of a fine pink crystalline powder. When quite cold, filter off, wash with a small quantity of cold water, and spread on a plate to dry. The salt so obtained is quite pure, and does not require further purification.

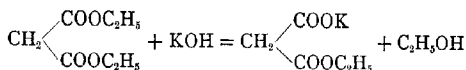
Other double salts can be prepared in a similar manner.

**Solution for Copper Coulommeter, and for Proof of Faraday's Law.**—Oettel recommends the following solution as being the most satisfactory for the coulommeter.

150 grm. crystallised copper sulphate.  
 50 „ sulphuric acid (conc.)  
 50 „ alcohol.  
 1 litre distilled water.

**Potassium Ethyl Malonate,**  $\text{CH}_2 \begin{cases} \text{COOC}_2\text{H}_5 \\ \text{COOK} \end{cases}$

—Add 160 grm. diethyl malonate to 130 c.c. alcohol, and to this solution add a concentrated alcoholic solution of 56 grm. potassium hydroxide.<sup>1</sup> This is half the quantity of potassium hydroxide necessary to hydrolyse the two ethyl groups



The mixture becomes warm, and the potassium salt is precipitated out, a semi-solid mass being obtained. Allow it to stand for three or four hours, and then evaporate nearly to dryness on the water bath, at the same time passing a rapid stream of carbonic acid gas through the mass.

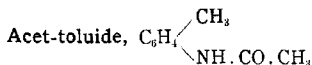
Now take up with just sufficient water to dissolve the solid substance, and if any unchanged diethyl malonate separates out, extract with a little ether, otherwise reduce again by evaporation to about one-third of its bulk. This mixture may now without further treatment be employed for electrolysis, in the preparation of diethyl succinate (p. 231).

**Potassium Ethyl Succinate,**  $\begin{array}{c} \text{CH}_2 - \text{COOC}_2\text{H}_5 \\ | \\ \text{CH}_2 - \text{COOK} \end{array}$

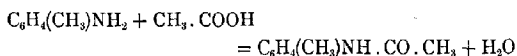
—Treat 174 grm. diethyl succinate, dissolved in 150 c.c. alcohol,

<sup>1</sup> This quantity assumes the potassium hydroxide to contain 100 per cent. KOH. If this is not the case, of course correspondingly larger quantities must be taken.

with a concentrated alcoholic solution of 56 grm. potassium hydroxide, exactly as described above in the preparation of potassium ethyl malonate. The concentrated solution of potassium ethyl succinate obtained at the end of the process may be employed, without further treatment, to prepare diethyl adipic acid (p. 231).



—Take 50 grm. of ortho-, para-, or meta-toluidine, and add to the toluidine about twice the theoretical quantity of glacial acetic acid to convert it into the acetyl compound



The mixture is contained in a flask, to which is fitted a long tube to act as a reflux condenser, placed on a sand bath, and heated to gentle boiling for from twelve to fifteen hours. It is then, while still hot, poured into cold water, and the more or less oily mixture allowed to stand overnight. It will by this time have solidified to a colourless or pinkish solid; this is filtered off, and washed with water until free from acetic acid. In order to further purify it, the acet-toluide may be recrystallised from alcohol.

#### NOTE TO P. 104.

Further experiment shows that the remarks made on page 104, in which the use of a gold electrode for the analysis of mercury is recommended, require to be modified. The first few results obtained with a gold electrode gave very fair results. Extended work, however, shows that the results obtained when this electrode is used are almost invariably from 1 to 2 per cent. too high. It has not up to the present been found possible to assign a reason for the abnormality, but the subject is still under investigation.

On the other hand, it has been found that the mercury adheres to a well-roughened (sand-blasted) flag-electrode, not in the form of globules, as is usually the case with a basin electrode, but in the form of a homogeneous amalgam, which may be washed with alcohol without in any way detracting from the accuracy of the results. The electrode amalgamates better after it has been used a few times. It is essential that it should be sand-blasted on the gauze as well as on the rim.

## Some Useful Data.

WHEN a current of 1 ampere intensity has passed through an electrolyte for 1 hour, 3600 coulombs of electricity have passed through the electrolyte.

A current of electricity of 1 ampere passing for 26.65 hours (in round numbers 27 hours) is equivalent to 96,540 coulombs or 1 faraday of electricity.

Twenty-seven ampere hours, *i.e.* a current of electricity of 1 ampere of intensity passing for 27 hours, will liberate the hydrogen equivalent of an element, *e.g.* 1 gm. of hydrogen, 8 gm. of oxygen, or 107.9 gm. of silver.

---

1 foot . . . .	= 30.47 cm.
1 inch. . . .	= 2.54 cm.
1 inch. . . .	= 25.40 mm.
1 metre . . . .	= 39.37 inches.
1 metre . . . .	= 3.28 feet.

---

1 lb. (avoirdupois)	= 7000 grains = 453.6 gm.
1 kilogram . . .	= 2.205 lbs.
1 ounce . . . .	= 28.35 gm.
1 gram . . . .	= 15.43 grains. <sup>†</sup>
1 grain . . . .	= 0.0648 gm.

---

- 1 cubic foot of water at 62° F. (16.6° C.) weighs 62.24 lbs.
- 1 cubic foot of water = 6.24 gals.
- 1 cwt. of water = 1.8 cubic feet = 11.2 gals.
- 1 ton of water = 35.9 cubic feet = 224 gals.
- 1 gallon = 0.1604 cubic foot = 10 lbs. water at 62° F. = 4.536 litres.



- 1 fluid ounce = 28.38 c.c.  
 1 cubic foot of air at 0° C. and 760 mm. pressure, weighs  
 0.0807 lb.  
 1 cubic foot of hydrogen at 0° C. and 760 mm. pressure, weighs  
 0.00559 lb.  
 1 atmosphere pressure = 14.7 lbs. per square inch = 2116 lbs.  
 per square foot = 760 mm. of mercury =  $10^6$  dynes  
 per square centimeter (approximately).  
 A column of water 2.3 feet high corresponds to a pressure of  
 1 lb. per square inch.  
 1 foot-pound =  $1.3562 \times 10^7$  ergs.  
 1 horse-power hour =  $33000 \times 60$  foot-pounds.  
 1 horse-power = 33000 foot-pounds per minute = 746 watts (see  
 p. 29).  
 1 kilowatt = 1.36 horse-power (see p. 29).  
 1 watt = 1 volt-ampere second (see p. 28).  
 1 kilowatt = 1000 watt hours.  
 volts  $\times$  amperes = watts.

---


$$\pi \dots\dots = 3.1416.$$

$$\frac{1}{\pi} \dots\dots = 0.3183.$$

$$\pi^3 \dots\dots = 9.8696.$$


---

The following formulæ will be found useful in calculating electrode surfaces:—

$$\text{Area of a circle} \dots = \pi r^2; \text{ or, (diameter)}^2 \times 0.7854.$$

$$\text{Volume of a cylinder} \dots = \pi r^2 L.$$

$$\text{Surface of a sphere} \dots = 4 \pi r^2.$$

$$\text{Volume of a sphere} \dots = \frac{4}{3} \pi r^3.$$

$$\text{Circumference of a circle} = \text{diam.} \times \pi \text{ or } r \times 2\pi.$$

$$\text{Diameter} \times 0.88623 \dots = \text{side of an equal square.}$$

$$\text{Diameter} \times 0.7071 \dots = \text{side of an inscribed square.}$$

$$\text{Circumference} \times 0.3183 = \text{diameter.}$$


---

Relation between Centigrade and Fahrenheit thermometric scales:—

$$\text{To find } F.^{\circ} = \frac{9}{5} C + 32$$

$$\text{To find } C.^{\circ} = (F - 32) \frac{5}{9}$$

1 litre of hydrogen at  $0^{\circ}$  C. and 760 mm. pressure, weighs 0.0896 grm. (0.09 approx.); this weight is called the **crith.**

The weight of 1 litre of any gas at N.T.P. is obtained by multiplying the density of the gas by the crith (0.0896 grm.).

11.2 litres of hydrogen at N.T.P. weigh 1 grm.

A gas expands 0.003665 ( $\frac{1}{273}$ ) of its volume for every degree through which it is heated.

The following formula is employed for calculating the volume of gas:—

$$v_0 = \frac{v}{1 + 0.003665t} \times \frac{p}{760}$$

where  $v_0$  is the volume at standard pressure, and  $v$  the volume of gas measured at pressure  $p$ , or by employing fractions

$$v_0 = \frac{v \times p \times 273}{760 \times (273 + t)}$$

#### NOTE TO CURVE, FIG. 64 (NEXT PAGE).

Attention has been called in several places in this book to the importance of knowing the electrode surface. The curve on the next page gives a ready way of finding both the area and the volume, and from the volume the weight of a wire electrode, the latter of which may be useful in purchasing platinum. The two following examples illustrate the manner of using the curve.

#### I. To find the area of the surface of a platinum wire 1.26 mm. diameter and 30 cm. long:—

Find the approximate position of the point 1.26 on the left vertical line, from this trace the imaginary horizontal line through the point 1.26 until it intersects the "area" line, and through the point of intersection trace a vertical line *downwards* and read its value on the *bottom horizontal line*. This is 0.395. This number represents the area of the surface of 1 cm. length of the wire in sq. cm. The total area is therefore  $0.395 \times 30 = 11.85$  sq. cm.

#### II. To find the volume of the same wire:—

Find the approximate position of the point 1.26 on the left vertical numbered line. Through this point follow an imaginary horizontal line until it intersects the "volume" curve, and through the point of intersection trace a vertical line *upwards* and read its value on the *top horizontal line*. This is 0.0125. This number is the volume of 1 cm. length of the wire, and the total volume of the wire, therefore, is  $0.0125 \times 30 = 0.375$  c.c.

The **weight** of this quantity of metal is found by multiplying the volume by the sp. gr. of the metal. *E.g.*, if the wire is platinum, the sp. gr. of which is 21.5, then the weight of the wire is  $0.375 \times 21.5 = 8.08$  grm.

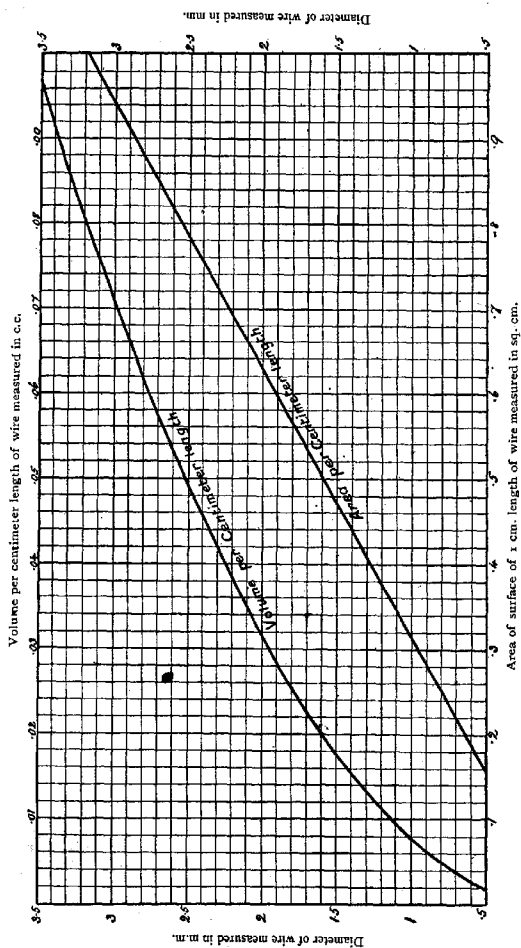


Fig. 64.  
Area of surface of 1 cm. length of wire measured in sq. cm.

TABLE IX.

## International Table of Atomic Weights.

	O = 16	H = 1		O = 16	H = 1
Aluminium . . Al	27.1	26.9	Neodymium . . Nd	143.6	142.5
Antimony . . . Sb	120.2	119.3	Neon . . . . . Ne	20.0	19.9
Argon . . . . . A	39.9	39.6	Nickel . . . . . Ni	58.7	58.3
Arsenic . . . . . As	75.0	74.4	Nitrogen . . . . N	14.04	13.93
Barium . . . . . Ba	137.4	136.4	Osmium . . . . . Os	191.0	189.6
Bismuth . . . . . Bi	208.5	206.9	Oxygen . . . . . O	16.0	15.88
Boron . . . . . B	11.0	10.9	Palladium . . . Pd	106.5	105.7
Bromine . . . . Br	79.96	79.36	Phosphorus . . P	31.0	30.77
Cadmium . . . . Cd	112.4	111.6	Platinum . . . . Pt	194.8	193.3
Cæsium . . . . . Cs	133.0	132.0	Potassium . . . K	39.15	38.86
Calcium . . . . . Ca	40.1	39.8	Praseodymium . Pr	140.5	139.4
Carbon . . . . . C	12.0	11.91			
Cerium . . . . . Ce	140.0	139.0	Radium . . . . . Ra	225.0	223.3
Chlorine . . . . Cl	35.45	35.18	Rhodium . . . . Rh	103.0	102.2
Chromium . . . . Cr	52.1	51.7	Rubidium . . . . Rb	85.5	84.9
Cobalt . . . . . Co	59.0	58.56	Ruthenium . . . Ru	101.7	100.9
Columbium . . .			Samarium . . . . Sm	150.3	149.2
(Niobium). Cb[Nb]	94.0	93.3	Scandium . . . . Sc	44.1	43.8
Copper . . . . . Cu	63.6	63.1	Selenium . . . . Se	79.2	78.6
Erbium . . . . . Er	166.0	164.8	Silicon . . . . . Si	28.4	28.2
Fluorine . . . . . F	19.0	18.9	Silver . . . . . Ag	107.93	107.12
Gadolinium . . . Gd	156.0	155.0	Sodium . . . . . Na	23.05	22.88
Gallium . . . . . Ga	70.0	69.5	Strontium . . . . Sr	87.6	86.94
Germanium . . . Ge	72.5	71.9	Sulphur . . . . . S	32.06	31.83
Glucinum . . . .			Tantalum . . . . Ta	183.0	181.6
(Beryllium) Gl[Be]	9.1	9.03	Tellurium . . . . Te	127.6	126.6
Gold . . . . . Au	197.2	195.7	Terbium . . . . . Tb	160.0	158.8
Helium . . . . . He	4.0	4.0	Thallium . . . . . Tl	204.1	202.6
Hydrogen . . . . H	1.008	1.000	Thorium . . . . . Th	232.5	230.8
Indium . . . . . In	115.0	114.1	Thulium . . . . . Tm	171.0	169.7
Iodine . . . . . I	126.97	126.01	Tin . . . . . Sn	119.0	118.1
Iridium . . . . . Ir	193.0	191.5	Titanium . . . . Ti	48.1	47.7
Iron . . . . . Fe	55.9	55.5	Tungsten . . . . W	184.0	182.6
Krypton . . . . . K	81.8	81.2	Uranium . . . . . U	238.5	236.7
Lanthanum . . . La	138.9	137.9	Vanadium . . . . V	51.2	50.8
Lead . . . . . Pb	206.9	205.35	Xenon . . . . . X	128.0	127.0
Lithium . . . . . Li	7.03	6.98	Ytterbium . . . . Yb	173.0	171.7
Magnesium . . . Mg	24.36	24.18	Yttrium . . . . . Yt	89.0	88.3
Manganese . . . . Mn	55.0	54.6	Zinc . . . . . Zn	65.4	64.9
Mercury . . . . . Hg	200.0	198.5	Zirconium . . . . Zr	90.6	89.9
Molybdenum . . Mo	96.0	95.3			

**TABLE X.**  
**Theoretical Percentage of the Metallic**  
**Elements in Some Metallic Compounds.**

Compound.	Formula.	Percentage of Metal.
Ammonio-stanni chloride . . . . .	$\text{SnCl}_4 \cdot 2\text{NH}_4\text{Cl}$	32.36 Sn
Ammonium aurichloride . . . . .	$(\text{NH}_4)_3\text{AuCl}_6 \cdot 3\text{H}_2\text{O}$	47.98 Au
Ammonium molybdate . . . . .	$(\text{NH}_4)_6\text{Mo}_7\text{O}_{21} \cdot 4\text{H}_2\text{O}$	54.36 Mo
Ammonium platini chloride . . . . .	$(\text{NH}_4)_2\text{PtCl}_6$	43.92 Pt
Antimonious oxide . . . . .	$\text{Sb}_2\text{O}_3$	71.34 Sb
Antimony tetroxide . . . . .	$\text{Sb}_2\text{O}_4$	78.84 Sb
Antimonyl potassium tartrate (tartar emetic) . . . . .	$\text{C}_4\text{H}_4\text{O}_6\text{K}(\text{SbO})_2 \cdot \frac{1}{2}\text{H}_2\text{O}$	36.16 Sb
Bismuth nitrate . . . . .	$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$	43.03 Bi
Bismuth oxide . . . . .	$\text{Bi}_2\text{O}_3$	86.69 Bi
Cadmium sulphate . . . . .	$\text{CdSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$	39.94 Cd
Cadmium sulphate . . . . .	$3\text{CdSO}_4 \cdot 8\frac{1}{2}\text{H}_2\text{O}$	42.77 Cd
Cobalt ammonium sulphate . . . . .	$(\text{NH}_4)_2\text{SO}_4 \cdot \text{CoSO}_4 \cdot 6\text{H}_2\text{O}$	14.94 Co
Cobalt chloride . . . . .	$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$	24.80 Co
Cobalt potassium sulphate . . . . .	$\text{K}_2\text{SO}_4 \cdot \text{CoSO}_4 \cdot 6\text{H}_2\text{O}$	13.49 Co
Cobalt sulphate . . . . .	$\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$	20.99 Co
Copper chloride . . . . .	$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	37.17 Cu
Copper sulphate . . . . .	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	25.33 Cu
Ferrous ammonium sulphate . . . . .	$(\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 6\text{H}_2\text{O}$	14.28 Fe
Ferrous sulphate . . . . .	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	21.18 Fe
Iron alum (ammonium) . . . . .	$\text{NH}_4\text{Fe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	11.62 Fe
Iron alum (potassium) . . . . .	$\text{KFe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	11.11 Fe
Lead nitrate . . . . .	$\text{Pb}(\text{NO}_3)_2$	62.52 Pb, 72.21 $\text{PbO}_2$
Manganese chloride . . . . .	$\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$	27.79 Mn
Manganese sulphate . . . . .	$\text{MnSO}_4 \cdot 7\text{H}_2\text{O}$	19.85 Mn
Mercuric chloride . . . . .	$\text{HgCl}_2$	73.82 Hg
Mercurous chloride . . . . .	$\text{Hg}_2\text{Cl}_2$	84.90 Hg
Molybdenum oxide (Molybdic acid) . . . . .	$\text{MoO}_3$	54.84 Mo
Nickel ammonium sulphate . . . . .	$(\text{NH}_4)_2\text{SO}_4 \cdot \text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	14.87 Ni
Nickel chloride . . . . .	$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	24.70 Ni
Nickel sulphate . . . . .	$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$	20.90 Ni
Nickel potassium sulphate . . . . .	$\text{K}_2\text{SO}_4 \cdot \text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	13.43 Ni
Potassium auri chloride . . . . .	$\text{KAuCl}_4 \cdot 3\text{H}_2\text{O}$	45.65 Au
Potassium permanganate . . . . .	$\text{KMnO}_4$	37.77 Mn
Potassium platini chloride . . . . .	$\text{K}_2\text{PtCl}_6$	39.93 Pt
Silver nitrate . . . . .	$\text{AgNO}_3$	63.51 Ag
Stannous chloride . . . . .	$\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$	41.84 Sn
Uranium oxide . . . . .	$\text{U}_3\text{O}_8$	83.72 U
Zinc sulphate . . . . .	$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	22.78 Zn

NOTE.—The percentages are calculated taking O = 16.

## THE USE OF LOGARITHMS.

\* Much of the arithmetical work required in quantitative chemistry may be simplified by the use of logarithms. Those in common use are calculated to the base 10, so that *the logarithm of a number is the power to which 10 is raised to obtain that number.*

For example, the logarithm of 100 is 2. This means that  $10^2 = 100$ . It is usually written  $\log 100 = 2$ . In the same way  $\log 1000 = 3$ , but the logarithms of numbers between 100 and 1000 lie between 2 and 3—that is, they are 2 plus a decimal quantity; e.g.  $\log 500 = 2.69897$ , because  $500 = 10^{2.69897}$ .

### To find the Logarithm of a Decimal Quantity.

$$0.05 = \frac{5}{100} = 5 \times 10^{-2} = 10^{0.69897} \times 10^{-2} = 10^{\bar{2}.69897}.$$

Therefore  $\log 0.05 = 2.69897$ , where  $\bar{2}$  is a negative quantity and 0.69897 is positive. It is convenient to keep it in this form.

The appended tables give the decimal portion, or **mantissa**, of the logarithm, and the integral portion, or **characteristic**, is obtained by inspection.

For numbers *greater than unity* the characteristic of the logarithm is *one less* than the number of figures in the integral portion of the number for which the logarithm is required. For example, to obtain  $\log 22.8$  look in the tables for the mantissa of  $\log 228$ , which is 0.35793. The characteristic is 1, therefore  $\log 22.8 = 1.35793$ . Likewise  $\log 2.28 = 0.35793$ .

For numbers *less than unity* the characteristic is obtained by *adding one* to the number of noughts between the decimal point and the *first significant figure*, and it is negative, e.g.  $\log 0.228 = \bar{1}.35793$  and  $\log 0.00228 = \bar{3}.35793$ .

To obtain  $\log 37\cdot376$ .—First consider the number 37376. On p. 303 look for 373 in the first column headed "Number," and its mantissa is given in the same horizontal row in the next column, headed "0," and is 57171. The mantissa for 3737 is given in the same horizontal row in the column headed "7," and is 57252. The next mantissa in the same row is that for 3738, and is 57264. For an increase of 1 in the fourth figure of the number the increase in the mantissa is 12. The fifth figure in the number represents tenths of a unit in the fourth place, so the same number of tenths of the difference between the mantissae of the first four figures (3737), and of that number increased by unity (3738), is added to the mantissa of the lower number (3737). These tenths are worked out in the column headed "Difference." The mantissa for  $\log 37376$  is  $57252 + 8\cdot4$  or  $57260\cdot4$  and  $\log 37\cdot376 = 1\cdot572604$ . In the same way  $\log 0\cdot0376 = 2\cdot572604$ .

To obtain  $\log 6$  or  $\log 0\cdot6$  look in the tables for the mantissa of  $\log 600$ , and to obtain  $\log 66$ , or  $\log 0\cdot66$ , look in the tables for the mantissa of  $\log 660$ . The characteristics are obtained by inspection according to rule.

$$\begin{array}{ll} \log 6 = 0\cdot77815 & \log 66 = 1\cdot81954 \\ \log 0\cdot6 = \bar{1}\cdot77815 & \log 6\cdot6 = 0\cdot81954 \\ \log 0\cdot006 = \bar{3}\cdot77815 & \log 0\cdot066 = \bar{2}\cdot81954 \end{array}$$

**To multiply two or more numbers together**, add the logarithms of the numbers, and the sum is the logarithm of the required product. **To divide a number by another**, subtract the logarithm of the divisor (or denominator of a fraction) from the logarithm of the dividend (or numerator of a fraction), and the difference is the logarithm of the quotient. The following examples illustrate the method of procedure.

**Example 1.**—Find the value of  $\frac{72\cdot968 \times 0\cdot078}{0\cdot3984}$

$$\begin{aligned} & \log \frac{72\cdot968 \times 0\cdot078}{0\cdot3984} \\ &= \log 72\cdot968 + \log 0\cdot078 - \log 0\cdot3984 \\ &= 1\cdot863128 + \bar{2}\cdot89209 - \bar{1}\cdot60032 \end{aligned}$$

$$= 0.755218 - 1.60032$$

$$= 1.154898$$

15473 is the mantissa for 1428

15503 " " " 1429

30 is the difference for 1

16.8 " " " 0.56

$\therefore$  154898 is the mantissa for 142856  
or correct to the fifth figure, 14286

As the characteristic is 1 the number of integral figures will be two, and 1.154898 is the logarithm of 14.286. The value of the fraction is therefore 14.286.

**Example 2.**—In the analysis of a sample of lead nitrate (p. 136) the following data were obtained.

Weight of basin electrode . . . . .	= 53.1814 gm.
" " " + lead nitrate	= 54.2228 "
" " " + deposit of $PbO_2$	= 53.9342 "

Find the percentage of lead in the lead nitrate.

$$\text{Weight of lead nitrate} = 1.0414 \text{ gm.}$$

$$\text{" " deposit of } PbO_2 = 0.7528 \text{ "}$$

238.9 gm. of  $PbO_2$  contain 206.9 gm. of Pb.

$\therefore$  the weight of lead in the deposit is  $\frac{0.7528 \times 206.9}{238.9}$  gm., and

this was obtained from 1.0412 gm. of  $Pb(NO_3)_2$ .

$$\therefore \text{ the percentage of lead} = \frac{100 \times 0.7528 \times 206.9}{1.0414 \times 238.9}$$

$$\log \frac{100 \times 0.7528 \times 206.9}{1.0414 \times 238.9}$$

$$= \log 100 + \log 0.7528 + \log 206.9 - \log 1.0414 - \log 238.9$$

$$= 2 + 1.87668 + 2.31576 - 0.017618 - 2.37822$$

$$= 4.19244 - 2.395838$$

$$= 1.796602$$



79657 is the mantissa for 6260

79664 " " " 6261

7 is the difference for 1

3.2 " " " 4 (approx.)

∴ 796602 is the mantissa for 62604

and 1.796602 is log 62.604

The percentage of lead is therefore **62.604**.

**Example 3.**—In the preparation of azobenzene (p. 241) according to the equation, 8 gm. of hydrogen will be required to reduce twice the gram-molecular weight of nitrobenzene to azobenzene. How many coulombs will be required to reduce 50 gm. of nitrobenzene?

The gram-molecular weight of nitrobenzene is 123.08;

∴ 8 gm. of hydrogen reduce  $2 \times 123.08$  gm. of nitrobenzene, and 8 gm. of hydrogen will be liberated by

$$96540 \times 8 \text{ coulombs (p. 7).}$$

∴ the quantity of electricity required to reduce  $2 \times 123.08$  gm. of nitrobenzene is  $96540 \times 8$  coulombs; and 50 gm. of nitrobenzene will require

$$\frac{96540 \times 8 \times 50}{2 \times 123.08} \text{ coulombs for reduction}$$

$$\log \frac{96540 \times 8 \times 50}{2 \times 123.08} = \log \frac{96540 \times 100}{61.54}$$

$$= \log 96540 + \log 100 - \log 61.54$$

$$= 4.98471 + 2 - 1.78916$$

$$= 5.19555$$

19535 is the mantissa for 1568

19562 " " " 1569

27 is the difference for 1

20 " " " 0.74

∴ 19555 is the mantissa for 156874

and 5.19555 is log 156874

∴ the quantity of electricity required is **156874 coulombs**.

**Example 4.**—From a gas coulometer 900 c.c. of a mixture of hydrogen and oxygen at 21° C. and 742 mm. was evolved. What quantity of electricity had passed through the coulometer? (See p. 15).

First find the volume of the mixed gases at N.T.P.

$$v_0 = \frac{900 \times 273 \times 742}{(273 + 21) \times 760} \quad (\text{See p. 287.})$$

1 ampere-hour, or 3600 coulombs, evolve 626.4 c.c. of the mixed gases at N.T.P. (see p. 15);

∴ the above quantity  $v_0$  will be evolved

$$\text{by } \frac{3600}{626.4} \times \frac{900 \times 273 \times 742}{(273 + 21) \times 760} \text{ coulombs.}$$

All operations of addition and subtraction must be performed before taking logarithms.

$$\begin{aligned} & \log \frac{3600 \times 900 \times 273 \times 742}{626.4 \times 294 \times 760} \\ &= \log 3600 + \log 900 + \log 273 + \log 742 \\ & \quad - \log 626.4 - \log 294 - \log 760 \\ &= 3.55630 + 2.95424 + 2.43616 + 2.87040 \\ & \quad - 2.79685 - 2.46835 - 2.88081 \\ &= 11.81710 - 8.14601 \\ &= 3.67109 \end{aligned}$$

67108 is the mantissa for 4689

67117 " " " " 4690

9 is the difference for 1

1 " " " " 0.1 (approx.).

67109 is the mantissa for 46891

$$\therefore 3.67109 \text{ is } \log 4689.1$$

∴ the quantity of electricity that had passed through the coulometer was **4689.1 coulombs.**

It is hoped that the above examples will be found sufficient to explain the use of logarithms even to those who may never

have employed them before. For further information upon the theory of the subject, students must study standard works upon algebra or trigonometry.

The following logarithm tables have been carefully checked, both against five-figure tables and seven-figure tables, and where any discrepancies were found, the numbers have been recalculated. I am greatly indebted to Mr. F. Hart, B.Sc., for kindly undertaking this laborious work, and also for calculating the worked-out examples on the preceding pages.

## FIVE-FIGURE LOGARITHMS

No.	Log. 0	1	2	3	4	5	6	7	8	9	Differences.			
100	00	000	043	087	130	173	217	260	303	346	389	44	48	42
101		432	475	518	561	604	647	689	732	775	817	1	4'4	4'2
102		860	903	945	988	030	072	115	157	199	242	2	8'8	8'4
103	01	284	326	368	410	452	494	536	578	620	662	3	13'2	12'9
104		703	745	787	828	870	912	953	995	036	078	4	17'6	17'2
105	02	119	160	202	243	284	325	366	407	449	490	5	22'0	21'5
106		531	572	612	653	694	735	776	816	857	898	6	26'4	25'8
107		938	979	019	060	100	141	181	222	262	302	7	30'8	30'1
108	03	342	383	423	463	503	543	583	623	663	703	8	35'2	34'3
109		743	782	822	862	902	941	981	021	060	100	9	39'6	37'8
110	04	139	179	218	258	297	336	376	415	454	493	41 40 39		
111		532	571	610	650	689	727	766	805	844	883	1	4'1	4'0
112		922	961	999	038	077	115	154	192	231	269	2	8'2	8'0
113	05	308	346	385	423	461	500	538	576	614	652	3	12'3	12'0
114		690	729	767	805	843	881	918	956	994	032	4	16'4	16'0
115	06	070	108	145	183	221	258	296	333	371	408	5	20'5	20'0
116		446	483	521	558	595	633	670	707	744	781	6	24'6	24'0
117		819	856	893	930	967	004	041	078	115	151	7	28'7	28'0
118	07	188	225	262	298	335	372	408	445	482	518	8	32'8	32'0
119		555	591	628	664	700	737	773	809	846	882	9	36'9	36'0
120		918	954	990	027	063	099	135	171	207	243	38 37 36		
121	08	279	314	350	386	422	458	493	529	565	600	1	3'8	3'7
122		636	672	707	743	778	814	849	884	920	955	2	7'6	7'4
123		991	026	061	096	132	167	202	237	272	307	3	11'4	11'1
124	09	342	377	412	447	482	517	552	587	621	656	4	15'2	14'8
125		691	726	760	795	830	864	899	934	968	003	5	19'0	18'5
126	10	037	072	106	140	175	209	243	278	312	346	6	22'8	22'2
127		380	415	449	483	517	551	585	619	653	687	7	26'6	25'9
128		721	755	789	823	856	890	924	958	992	026	8	30'4	29'6
129	11	059	098	126	160	193	227	260	294	327	361	9	34'2	33'3
130		394	428	461	494	528	561	594	628	661	694	35 34 33		
131		727	760	793	826	860	893	926	959	992	024	1	3'5	3'4
132	12	057	090	123	156	189	222	254	287	320	352	2	7'0	6'8
133		385	418	450	483	516	548	581	613	646	678	3	10'5	10'2
134		710	743	775	808	840	872	905	937	969	001	4	14'0	13'6
135	13	033	066	098	130	162	194	226	258	290	322	5	17'5	17'0
136		354	386	418	450	481	513	545	577	609	640	6	21'0	20'4
137		672	704	735	767	799	830	862	893	925	956	7	24'5	23'8
138		988	019	051	082	114	145	176	208	239	270	8	28'0	27'2
139	14	301	333	364	395	426	457	489	520	551	582	9	31'5	30'6
140		613	644	675	706	737	768	799	829	860	891	32 31		
141		922	953	983	014	045	076	106	137	168	198	1	3'2	3'1
142	15	229	259	290	320	351	381	412	442	473	503	2	6'4	6'2
143		534	564	594	625	655	685	715	746	776	806	3	9'6	9'3
144		836	866	897	927	957	987	017	047	077	107	4	12'8	12'4
145	16	137	167	197	227	256	286	316	346	376	406	5	16'0	15'5
146		435	465	495	524	554	584	613	643	673	702	6	19'2	18'6
147		732	761	791	820	850	879	909	938	967	997	7	22'4	21'7
148	17	026	056	085	114	143	173	202	231	260	289	8	25'6	24'8
149		319	348	377	406	435	464	493	522	551	580	9	28'8	27'9

No.	Log.	0	1	2	3	4	5	6	7	8	9	Differences.	
150	17	609.638	667	696	725	754	782	811	840	869		30	29
151		898	926	955	984	013	041	070	099	127	156	1	3.0
152	18	184	213	241	270	298	327	355	384	412	441	2	6.0
153		469	498	526	554	583	611	639	667	696	724	3	9.0
154		752	780	808	837	865	893	921	949	977	005	4	12.0
155	19	033	061	089	117	145	173	201	229	257	285	5	15.0
156		312	340	368	396	424	451	479	507	535	562	6	18.0
157		590	618	645	673	700	728	756	783	811	838	7	21.0
158		866	893	921	948	976	003	030	058	085	112	8	24.0
159	20	140	167	194	222	249	276	303	330	358	385	9	27.0
160		412	439	466	493	520	548	575	602	629	656	28	
161		683	710	737	763	790	817	844	871	898	925	1	2.8
162		952	978	005	032	059	085	112	139	165	192	2	5.6
163	21	219	245	272	299	325	352	378	405	431	458	3	8.4
164		484	511	537	564	590	617	643	669	696	722	4	11.2
165		748	775	801	827	854	880	906	932	958	985	5	14.0
166	22	011	037	063	089	115	141	167	194	220	246	6	16.8
167		272	298	324	350	376	401	427	453	479	505	7	19.6
168		531	557	583	608	634	660	686	712	737	763	8	22.4
169		789	814	840	866	891	917	943	968	994	019	9	25.2
170	23	045	070	096	121	147	172	198	223	249	274	26	
171		300	325	350	376	401	426	452	477	502	528	1	2.6
172		553	578	603	629	654	679	704	729	754	779	2	5.2
173		805	830	855	880	905	930	955	980	005	030	3	7.8
174	24	055	080	105	130	155	180	204	229	254	279	4	10.4
175		304	329	353	378	403	428	452	477	502	527	5	13.0
176		551	576	601	625	650	674	699	724	748	773	6	15.6
177		797	822	846	871	895	920	944	969	993	018	7	18.2
178	25	042	066	091	115	139	164	188	212	237	261	8	20.8
179		285	310	334	358	382	406	431	455	479	503	9	23.4
180		527	551	575	600	624	648	672	696	720	744	24	
181		768	792	816	840	864	888	912	935	959	983	1	2.4
182	26	007	031	055	079	102	126	150	174	198	221	2	4.8
183		245	269	293	316	340	364	387	411	435	458	3	7.2
184		482	505	529	553	576	600	623	647	670	694	4	9.6
185		717	741	764	788	811	834	858	881	905	928	5	12.0
186		951	975	998	021	045	068	091	114	138	161	6	14.4
187	27	184	207	231	254	277	300	323	346	370	393	7	16.8
188		416	439	462	485	508	531	554	577	600	623	8	19.2
189		646	669	692	715	738	761	784	807	830	852	9	21.6
190		875	898	921	944	967	989	012	035	058	081	22	
191	28	103	126	149	171	194	217	240	262	285	307	1	2.2
192		330	353	375	398	421	443	466	488	511	533	2	4.4
193		556	578	601	623	646	668	691	713	735	758	3	6.6
194		780	803	825	847	870	892	914	937	959	981	4	8.8
195	29	003	026	048	070	092	115	137	159	181	203	5	11.0
196		226	248	270	292	314	336	358	380	403	425	6	13.2
197		447	469	491	513	535	557	579	601	623	645	7	15.4
198		667	688	710	732	754	776	798	820	842	863	8	17.6
199		885	907	929	951	973	994	016	038	060	081	9	19.8

No.	Log.	0	1	2	3	4	5	6	7	8	9	Differences.
200	<b>30</b>	108	125	146	168	190	211	233	255	276	298	21
201		320	341	363	384	406	428	449	471	492	514	1 2'1
202		535	557	578	600	621	642	664	685	707	728	2 4'2
203		750	771	792	814	835	856	878	899	920	942	3 6'3
204		963	984	006	027	048	069	091	112	133	154	4 8'4
205	<b>31</b>	175	197	218	239	260	281	302	323	345	366	5 10'5
206		387	408	429	450	471	492	513	534	555	576	6 12'6
207		597	618	639	660	681	702	723	744	765	785	7 14'7
208		806	827	848	869	890	911	931	952	973	994	8 16'8
209	<b>32</b>	015	035	056	077	098	118	139	160	181	201	9 18'9
210		222	243	263	284	305	325	346	366	387	408	20
211		428	449	469	490	510	531	552	572	593	613	1 2'0
212		634	654	675	695	715	736	756	777	797	818	2 4'0
213		838	858	879	899	919	940	960	980	001	021	3 6'0
214	<b>33</b>	041	062	082	102	122	143	163	183	203	224	4 8'0
215		244	264	284	304	325	345	365	385	405	425	5 10'0
216		445	465	486	506	526	546	566	586	606	626	6 12'0
217		646	666	686	706	726	746	766	786	806	826	7 14'0
218		846	866	885	905	925	945	965	985	005	025	8 16'0
219	<b>34</b>	044	064	084	104	124	143	163	183	203	223	9 18'0
220		242	262	282	301	321	341	361	380	400	420	1 1'9
221		439	459	479	498	518	537	557	577	596	616	2 3'8
222		635	655	674	694	713	733	753	772	792	811	3 5'7
223		830	850	869	889	908	928	947	967	986	006	4 7'6
224	<b>35</b>	025	044	064	083	102	122	141	160	180	199	5 9'5
225		218	238	257	276	295	315	334	353	372	392	6 11'4
226		411	430	449	468	488	507	526	545	564	583	7 13'3
227		603	622	641	660	679	698	717	736	755	774	8 15'2
228		793	813	832	851	870	889	908	927	946	965	9 17'1
229		984	003	021	040	059	078	097	116	135	154	1 1'8
230	<b>36</b>	173	192	211	229	248	267	286	305	324	342	2 3'6
231		361	380	399	418	436	455	474	493	511	530	3 5'4
232		549	568	586	605	624	642	661	680	698	717	4 7'2
233		736	754	773	791	810	829	847	866	884	903	5 9'0
234		922	940	959	977	996	014	033	051	070	088	6 10'8
235	<b>37</b>	107	125	144	162	181	199	218	236	254	273	7 12'6
236		291	310	328	346	365	383	401	420	438	457	8 14'4
237		475	493	511	530	548	566	585	603	621	639	9 16'2
238		658	676	694	712	731	749	767	785	803	822	1 1'8
239		840	858	876	894	912	931	949	967	985	003	2 3'6
240	<b>38</b>	021	039	057	075	093	112	130	148	166	184	3 5'4
241		202	220	238	256	274	292	310	328	346	364	4 7'2
242		382	399	417	435	453	471	489	507	525	543	5 9'0
243		561	578	596	614	632	650	668	686	703	721	6 10'8
244		739	757	775	792	810	828	846	863	881	899	7 12'6
245		917	934	952	970	987	005	023	041	058	076	8 14'4
246	<b>39</b>	094	111	129	146	164	182	199	217	235	252	9 16'2
247		270	287	305	322	340	358	375	393	410	428	
248		445	463	480	498	515	533	550	568	585	602	
249		620	637	655	672	690	707	724	742	759	777	

No.	Log. 0	1	2	3	4	5	6	7	8	9	Differences.	
250	39	794	811	829	846	863	881	898	915	933	950	
251		967	985	002	019	037	054	071	088	106	123	18
252	40	140	157	175	192	209	226	243	261	278	295	1 1'8
253		312	329	346	364	381	398	415	432	449	466	2 3'6
254		483	500	518	535	552	569	586	603	620	637	3 5'4
255		654	671	688	705	722	739	756	773	790	807	4 7'2
256		824	841	858	875	892	909	926	943	959	976	5 9'0
257		993	010	027	044	061	078	095	111	128	145	6 10'8
258	41	162	179	196	212	229	246	263	280	296	313	7 12'6
259		330	347	363	380	397	414	430	447	464	481	8 14'4
260		497	514	531	547	564	581	597	614	631	647	9 16'2
261		664	681	697	714	731	747	764	780	797	814	
262		830	847	863	880	896	913	929	946	963	979	
263		996	012	029	045	062	078	095	111	127	144	
264	42	160	177	193	210	226	243	259	275	292	308	17
265		325	341	357	374	390	406	423	439	455	472	1 1'7
266		488	504	521	537	553	570	586	602	619	635	2 3'4
267		651	667	684	700	716	732	749	765	781	797	3 5'1
268		813	830	846	862	878	894	911	927	943	959	4 6'8
269		975	991	008	024	040	056	072	088	104	120	5 8'5
270	43	136	152	169	185	201	217	233	249	265	281	6 10'2
271		297	313	329	345	361	377	393	409	425	441	7 11'9
272		457	473	489	505	521	537	553	569	584	600	8 13'6
273		616	632	648	664	680	696	712	727	743	759	9 15'3
274		775	791	807	823	838	854	870	886	902	917	
275		933	949	965	981	996	012	028	044	059	075	
276	44	091	107	122	138	154	170	185	201	217	232	16
277		248	264	279	295	311	326	342	358	373	389	
278		404	420	436	451	467	483	498	514	529	545	1 1'6
279		560	576	592	607	623	638	654	669	685	700	2 3'2
280		716	731	747	762	778	793	809	824	840	855	3 4'8
281		871	886	902	917	932	948	963	979	994	010	4 6'4
282	45	025	040	056	071	086	102	117	133	148	163	5 8'0
283		179	194	209	225	240	255	271	286	301	317	6 9'6
284		332	347	362	378	393	408	423	439	454	469	7 11'2
285		484	500	515	530	545	561	576	591	606	621	8 12'8
286		637	652	667	682	697	712	728	743	758	773	9 14'4
287		788	803	818	834	849	864	879	894	909	924	
288		939	954	969	984	000	015	030	045	060	075	
289	46	090	105	120	135	150	165	180	195	210	225	15
290		240	255	270	285	300	315	330	344	359	374	
291		389	404	419	434	449	464	479	494	509	523	1 1'5
292		538	553	568	583	598	613	627	642	657	672	2 3'0
293		687	702	716	731	746	761	776	790	805	820	3 4'5
294		835	850	864	879	894	909	923	938	953	967	4 6'0
295		982	997	012	026	041	056	070	085	100	114	5 7'5
296	47	129	144	159	173	188	202	217	232	246	261	6 9'0
297		276	290	305	319	334	349	363	378	392	407	7 10'5
298		422	436	451	465	480	494	509	524	538	553	8 12'0
299		567	582	596	611	625	640	654	669	683	698	9 13'5



No.	Log.	0	1	2	3	4	5	6	7	8	9	Difference.
300	47	712	727	741	756	770	784	799	813	828	842	
301		857	871	885	900	914	929	943	958	972	986	
302	48	001	015	029	044	058	073	087	101	116	130	
303		144	159	173	187	202	216	230	244	259	273	
304		287	302	316	330	344	359	373	387	401	416	
305		480	444	458	473	487	501	515	530	544	558	
306		572	586	601	615	629	643	657	671	686	700	
307		714	728	742	756	770	785	799	813	827	841	
308		855	869	883	897	911	926	940	954	968	982	
309		996	010	024	038	052	066	080	094	108	122	
310	49	136	150	164	178	192	206	220	234	248	262	14
311		276	290	304	318	332	346	360	374	388	402	1
312		415	429	443	457	471	485	499	513	527	541	2
313		554	568	582	596	610	624	638	651	665	679	3
314		693	707	721	734	748	762	776	790	803	817	4
315		831	845	859	872	886	900	914	927	941	955	5
316		969	982	996	010	024	037	051	065	079	092	6
317	50	106	120	133	147	161	174	188	202	215	229	7
318		243	256	270	284	297	311	325	338	352	365	8
319		379	393	406	420	433	447	461	474	488	501	9
320		515	529	542	556	569	583	596	610	623	637	
321		650	664	678	691	705	718	732	745	759	772	
322		786	799	813	826	839	853	866	880	893	907	
323		920	934	947	961	974	987	001	014	028	041	
324	51	054	068	081	095	108	121	135	148	162	175	
325		188	202	215	228	242	255	268	282	295	308	
326		322	335	348	362	375	388	402	415	428	441	
327		455	468	481	495	508	521	534	548	561	574	
328		587	601	614	627	640	654	667	680	693	706	
329		720	733	746	759	772	786	799	812	825	838	
330		851	865	878	891	904	917	930	943	957	970	13
331		983	996	009	022	035	048	061	075	088	101	1
332	52	114	127	140	153	166	179	192	205	218	231	2
333		244	257	270	284	297	310	323	336	349	362	3
334		375	388	401	414	427	440	453	466	479	492	4
335		504	517	530	543	556	569	582	595	608	621	5
336		634	647	660	673	686	699	711	724	737	750	6
337		763	776	789	802	815	827	840	853	866	879	7
338		892	905	917	930	943	956	969	982	994	007	8
339	53	020	033	046	058	071	084	097	110	122	135	9
340		148	161	173	186	199	212	224	237	250	263	
341		275	288	301	314	326	339	352	364	377	390	
342		403	415	428	441	453	466	479	491	504	517	
343		529	542	555	567	580	593	605	618	631	643	
344		656	668	681	694	706	719	732	744	757	769	
345		782	794	807	820	832	845	857	870	882	895	
346		908	920	933	945	958	970	983	995	008	020	
347	54	033	045	058	070	083	095	108	120	133	145	
348		158	170	183	195	208	220	233	245	258	270	
349		283	295	307	320	332	345	357	370	382	394	

No.	Log.	0	1	2	3	4	5	6	7	8	9	Differences.
350	54	407	419	432	444	456	469	481	494	506	518	
351		531	543	555	568	580	593	605	617	630	642	
352		654	667	679	691	704	716	728	741	753	765	
353		777	790	802	814	827	839	851	864	876	888	
354		900	913	925	937	949	962	974	986	998	011	13
355	55	023	035	047	060	072	084	096	108	121	133	1 1'3
356		145	157	169	182	194	206	218	230	242	255	2 2'6
357		267	279	291	303	315	328	340	352	364	376	3 3'9
358		388	400	413	425	437	449	461	473	485	497	4 5'2
359		509	522	534	546	558	570	582	594	606	618	5 6'5
360		630	642	654	666	678	691	703	715	727	739	6 7'8
361		751	763	775	787	799	811	823	835	847	859	7 9'1
362		871	883	895	907	919	931	943	955	967	979	8 10'4
363		991	003	015	027	038	050	062	074	086	098	9 11'7
364	56	110	122	134	146	158	170	182	194	205	217	
365		229	241	253	265	277	289	301	312	324	336	
366		348	360	372	384	396	407	419	431	443	455	
367		467	478	490	502	514	526	538	549	561	573	
368		585	597	608	620	632	644	656	667	679	691	
369		703	714	726	738	750	761	773	785	797	808	12
370		820	832	844	855	867	879	891	902	914	926	1 1'2
371		937	949	961	972	984	996	008	019	031	043	2 2'4
372	57	054	066	078	089	101	113	124	136	148	159	3 3'6
373		171	183	194	206	217	229	241	252	264	276	4 4'8
374		287	299	310	322	334	345	357	368	380	392	5 6'0
375		403	415	426	438	449	461	473	484	496	507	6 7'2
376		519	530	542	553	565	576	588	600	611	623	7 8'4
377		634	646	657	669	680	692	703	715	726	738	8 9'6
378		749	761	772	784	795	807	818	830	841	852	9 10'8
379		864	875	887	898	910	921	933	944	955	967	
380		978	990	001	013	024	035	047	058	070	081	
381	58	092	104	115	127	138	149	161	172	184	195	
382		206	218	229	240	252	263	274	286	297	309	
383		320	331	343	354	365	377	388	399	410	422	
384		433	444	456	467	478	490	501	512	524	535	11
385		546	557	569	580	591	602	614	625	636	647	1 1'1
386		659	670	681	692	704	715	726	737	749	760	2 2'2
387		771	782	794	805	816	827	838	850	861	872	3 3'3
388		883	894	906	917	928	939	950	961	973	984	4 4'4
389		995	006	017	028	040	051	062	073	084	095	5 5'5
390	59	106	118	129	140	151	162	173	184	195	207	6 6'6
391		218	229	240	251	262	273	284	295	306	318	
392		329	340	351	362	373	384	395	406	417	428	7 7'7
393		439	450	461	472	483	494	506	517	528	539	8 8'8
394		550	561	572	583	594	605	616	627	638	649	9 9'9
395		660	671	682	693	704	715	726	737	748	759	
396		770	780	791	802	813	824	835	846	857	868	
397		879	890	901	912	923	934	945	956	966	977	
398		988	999	010	021	032	043	054	065	076	086	
399	60	097	108	119	130	141	152	163	173	184	195	

No.	Log. 0	1	2	3	4	5	6	7	8	9	Differences.	
400	60	206	217	228	239	249	260	271	282	293	304	
401		314	325	336	347	358	369	379	390	401	412	
402		423	433	444	455	466	477	487	498	509	520	
403		530	541	552	563	574	584	595	606	617	627	
404		638	649	660	670	681	692	703	713	724	735	
405		745	756	767	778	788	799	810	820	831	842	
406		853	863	874	885	895	906	917	927	938	949	
407		959	970	981	991	002	013	023	034	045	055	
408	61	066	077	087	098	109	119	130	140	151	162	
409		172	183	194	204	215	225	236	247	257	268	
410		278	289	300	310	321	331	342	352	363	374	
411		384	395	405	416	426	437	448	458	469	479	
412		490	500	511	521	532	542	553	563	574	584	
413		595	606	616	627	637	648	658	669	679	690	
414		700	711	721	731	742	752	763	773	784	794	
415		805	815	826	836	847	857	868	878	888	899	
416		909	920	930	941	951	961	972	982	993	003	
417	62	014	024	034	045	055	066	076	086	097	107	
418		118	128	138	149	159	170	180	190	201	211	
419		221	232	242	252	263	273	284	294	304	315	
420		325	335	346	356	366	377	387	397	408	418	
421		428	439	449	459	469	480	490	500	511	521	
422		531	542	552	562	572	583	593	603	613	624	
423		634	644	655	665	675	685	696	706	716	726	
424		737	747	757	767	778	788	798	808	818	829	
425		839	849	859	870	880	890	900	910	921	931	
426		941	951	961	972	982	992	002	012	022	033	
427	63	043	053	063	073	083	094	104	114	124	134	
428		144	155	165	175	185	195	205	215	225	236	
429		246	256	266	276	286	296	306	317	327	337	
430		347	357	367	377	387	397	407	417	428	438	
431		448	458	468	478	488	498	508	518	528	538	
432		548	558	568	579	589	599	609	619	629	639	
433		649	659	669	679	689	699	709	719	729	739	
434		749	759	769	779	789	799	809	819	829	839	
435		849	859	869	879	889	899	909	919	929	939	
436		949	959	969	979	988	998	008	018	028	038	
437	64	048	058	068	078	088	098	108	118	128	137	
438		147	157	167	177	187	197	207	217	227	237	
439		246	256	266	276	286	296	306	316	326	335	
440		345	355	365	375	385	395	404	414	424	434	
441		444	454	464	473	483	493	503	513	523	532	
442		542	552	562	572	582	591	601	611	621	631	
443		640	650	660	670	680	689	699	709	719	729	
444		738	748	758	768	777	787	797	807	816	826	
445		836	846	856	865	875	885	895	904	914	924	
446		933	943	953	963	972	982	992	002	011	021	
447	65	031	040	050	060	070	079	089	099	108	118	
448		128	137	147	157	167	176	186	196	205	215	
449		225	234	244	254	263	273	283	292	302	312	

No.	Log. 0	1	2	3	4	5	6	7	8	9	Differences.	
450	65	321	331	341	350	360	369	379	389	398	408	
451		418	427	437	447	456	466	475	485	495	504	
452		514	523	533	543	552	562	571	581	591	600	
453		610	619	629	639	648	658	667	677	686	696	
454		706	715	725	734	744	753	763	772	782	792	
455		801	811	820	830	839	849	858	868	877	887	
456		896	906	916	925	935	944	954	963	973	982	
457		992	001	011	020	030	039	049	058	068	077	
458	66	087	096	106	115	124	134	143	153	162	172	
459		181	191	200	210	219	229	238	247	257	266	
460		276	285	295	304	314	323	332	342	351	361	10
461		370	380	389	398	408	417	427	436	445	455	1 1'0
462		464	474	483	492	502	511	521	530	539	549	2 2'0
463		558	567	577	586	596	605	614	624	633	642	3 3'0
464		652	661	671	680	689	699	708	717	727	736	4 4'0
465		745	755	764	773	783	792	801	811	820	829	5 5'0
466		839	848	857	867	876	885	894	904	913	922	6 6'0
467		932	941	950	960	969	978	987	997	006	015	7 7'0
468	67	025	034	043	052	062	071	080	089	099	108	8 8'0
469		117	127	136	145	154	164	173	182	191	201	9 9'0
470		210	219	228	237	247	256	265	274	284	293	
471		302	311	321	330	339	348	357	367	376	385	
472		394	403	413	422	431	440	449	459	468	477	
473		486	495	504	514	523	532	541	550	560	569	
474		578	587	596	605	614	624	633	642	651	660	
475		669	678	688	697	706	715	724	733	742	752	
476		761	770	779	788	797	806	815	825	834	843	
477		852	861	870	879	888	897	906	916	925	934	
478		943	952	961	970	979	988	997	006	015	024	
479	68	034	043	052	061	070	079	088	097	106	115	9
480		124	133	142	151	160	169	178	187	196	205	1 0'9
481		215	224	233	242	251	260	269	278	287	296	2 1'8
482		305	314	323	332	341	350	359	368	377	386	3 2'7
483		395	404	413	422	431	440	449	458	467	476	4 3'0
484		485	494	502	511	520	529	538	547	556	565	5 4'5
485		574	583	592	601	610	619	628	637	646	655	6 5'4
486		664	673	681	690	699	708	717	726	735	744	7 6'3
487		753	762	771	780	789	797	806	815	824	833	8 7'2
488		842	851	860	869	878	886	895	904	913	922	9 8'1
489		931	940	949	958	966	975	984	993	002	011	
490	69	020	028	037	046	055	064	073	082	090	099	
491		108	117	126	135	144	152	161	170	179	188	
492		197	205	214	223	232	241	249	258	267	276	
493		285	294	302	311	320	329	338	346	355	364	
494		373	381	390	399	408	417	425	434	443	452	
495		461	469	478	487	496	504	513	522	531	539	
496		548	557	566	574	583	592	601	609	618	627	
497		636	644	653	662	671	679	688	697	705	714	
498		723	732	740	749	758	767	775	784	793	801	
499		810	819	827	836	845	854	862	871	880	888	

No.	Log.	0	1	2	3	4	5	6	7	8	9	Differences.
500	<b>69</b>	897	906	914	923	932	940	949	958	966	975	
501		984	992	001	010	018	027	036	044	053	062	
502	<b>70</b>	070	079	088	096	105	114	122	131	140	148	
503		157	165	174	183	191	200	209	217	226	234	
504		243	252	260	269	278	286	295	303	312	321	
505		329	338	346	355	364	372	381	389	398	406	
506		415	424	432	441	449	458	467	475	484	492	
507		501	509	518	526	535	544	552	561	569	578	
508		586	595	603	612	621	629	638	646	655	663	
509		672	680	689	697	706	714	723	731	740	748	
510		757	766	774	783	791	800	808	817	825	834	
511		842	851	859	868	876	885	893	902	910	919	
512		927	935	944	952	961	969	978	986	995	003	
513	<b>71</b>	012	020	029	037	046	054	062	071	079	088	
514		096	105	113	122	130	139	147	155	164	172	
515		181	189	198	206	214	223	231	240	248	257	
516		265	273	282	290	299	307	315	324	332	341	
517		349	357	366	374	383	391	399	408	416	425	
518		433	441	450	458	466	475	483	492	500	508	
519		517	525	533	542	550	559	567	575	584	592	
520		600	609	617	625	634	642	650	659	667	675	
521		684	692	700	709	717	725	734	742	750	759	
522		767	775	784	792	800	809	817	825	834	842	
523		850	858	867	875	883	892	900	908	917	925	
524		933	941	950	958	966	975	983	991	999	008	
525	<b>72</b>	016	024	032	041	049	057	066	074	082	090	
526		099	107	115	123	132	140	148	156	165	173	
527		181	189	198	206	214	222	230	239	247	255	
528		263	272	280	288	296	304	313	321	329	337	
529		346	354	362	370	378	387	395	403	411	419	
530		428	436	444	452	460	469	477	485	493	501	
531		509	518	526	534	542	550	558	567	575	583	
532		591	599	607	616	624	632	640	648	656	665	
533		673	681	689	697	705	713	722	730	738	746	
534		754	762	770	779	787	795	803	811	819	827	
535		835	843	852	860	868	876	884	892	900	908	
536		916	925	933	941	949	957	965	973	981	989	
537		997	006	014	022	030	038	046	054	062	070	
538	<b>73</b>	078	086	094	102	111	119	127	135	143	151	
539		159	167	175	183	191	199	207	215	223	231	
540		239	247	255	263	272	280	288	296	304	312	
541		320	328	336	344	352	360	368	376	384	392	
542		400	408	416	424	432	440	448	456	464	472	
543		480	488	496	504	512	520	528	536	544	552	
544		560	568	576	584	592	600	608	616	624	632	
545		640	648	656	664	672	679	687	695	703	711	
546		719	727	737	743	751	759	767	775	783	791	
547		799	807	815	823	830	838	846	854	862	870	
548		878	886	894	902	910	918	926	933	941	949	
549		957	965	973	981	989	997	005	013	020	028	

No.	Log. 0	1	2	3	4	5	6	7	8	9	Differences.	
550	74	036	044	052	060	068	076	084	092	099	107	
551		115	123	131	139	147	155	162	170	178	186	
552		194	202	210	217	225	233	241	249	257	265	
553		273	280	288	296	304	312	320	327	335	343	
554		351	359	367	374	382	390	398	406	414	421	
555		429	437	445	453	461	468	476	484	492	500	
556		507	515	523	531	539	547	554	562	570	578	
557		586	593	601	609	617	624	632	640	648	656	
558		663	671	679	687	695	702	710	718	726	733	
559		741	749	757	764	772	780	788	796	803	811	
560		819	827	834	842	850	858	865	873	881	889	8
561		896	904	912	920	927	935	943	950	958	966	1 0'8
562		974	981	989	997	005	012	020	028	035	043	2 1'6
563	75	051	059	066	074	082	089	097	105	113	120	3 2'4
564		128	136	143	151	159	166	174	182	189	197	4 3'2
565		205	213	220	228	236	243	251	259	266	274	5 4'0
566		282	289	297	305	312	320	328	335	343	351	6 4'8
567		358	366	374	381	389	397	404	412	420	427	7 5'6
568		435	442	450	458	465	473	481	488	496	504	8 6'4
569		511	519	526	534	542	549	557	565	572	580	9 7'2
570		587	595	603	610	618	626	633	641	648	656	
571		664	671	679	686	694	702	709	717	724	732	
572		740	747	755	762	770	778	785	793	800	808	
573		815	823	831	838	846	853	861	868	876	884	
574		891	899	906	914	921	929	937	944	952	959	
575		967	974	982	989	997	005	012	020	027	035	
576	76	042	050	057	065	072	080	087	095	103	110	
577		118	125	133	140	148	155	163	170	178	185	
578		193	200	208	215	223	230	238	245	253	260	
579		268	275	283	290	298	305	313	320	328	335	
580		343	350	358	365	373	380	388	395	403	410	7
581		418	425	433	440	447	455	462	470	477	485	1 0'7
582		492	500	507	515	522	530	537	544	552	559	2 1'4
583		567	574	582	589	597	604	612	619	626	634	3 2'1
584		641	649	656	664	671	678	686	693	701	708	4 2'8
585		716	723	730	738	745	753	760	768	775	782	5 3'5
586		790	797	805	812	819	827	834	842	849	856	6 4'2
587		864	871	879	886	893	901	908	916	923	930	7 4'9
588		938	945	952	960	967	975	982	989	997	004	8 5'6
589	77	012	019	026	034	041	048	056	063	070	078	9 6'3
590		085	093	100	107	115	122	129	137	144	151	
591		159	166	173	181	188	195	203	210	217	225	
592		232	240	247	254	262	269	276	283	291	298	
593		305	313	320	327	335	342	349	357	364	371	
594		379	386	393	401	408	415	422	430	437	444	
595		452	459	466	474	481	488	495	503	510	517	
596		525	532	539	546	554	561	568	576	583	590	
597		597	605	612	619	627	634	641	648	656	663	
598		670	677	685	692	699	706	714	721	728	735	
599		743	750	757	764	772	778	786	793	801	808	

No.	Log. 0	1	2	3	4	5	6	7	8	9	Differences.
600	815	822	830	837	844	851	859	866	873	880	
601	887	895	902	909	916	924	931	938	945	952	
602	960	967	974	981	988	996	003	010	017	025	
603	78 032	039	046	053	061	068	075	082	089	096	
604	104	111	118	125	132	140	147	154	161	168	
605	176	183	190	197	204	211	219	226	233	240	
606	247	254	262	269	276	283	290	297	305	312	
607	319	326	333	340	347	355	362	369	376	383	
608	390	397	405	412	419	426	433	440	447	455	
609	462	469	476	483	490	497	504	512	519	526	
610	538	540	547	554	561	569	576	583	590	597	7
611	604	611	618	625	633	640	647	654	661	668	1 0'7
612	675	682	689	696	704	711	718	725	732	739	2 1'4
613	746	753	760	767	774	781	789	796	803	810	3 2'1
614	817	824	831	838	845	852	859	866	873	880	4 2'8
615	888	895	902	909	916	923	930	937	944	951	5 3'5
616	958	965	972	979	986	993	000	007	014	021	6 4'2
617	79 029	036	043	050	057	064	071	078	085	092	7 4'9
618	099	106	113	120	127	134	141	148	155	162	8 5'6
619	169	176	183	190	197	204	211	218	225	232	9 6'3
620	239	246	253	260	267	274	281	288	295	302	
621	309	316	323	330	337	344	351	358	365	372	
622	379	386	393	400	407	414	421	428	435	442	
623	449	456	463	470	477	484	491	498	505	511	
624	518	525	532	539	546	553	560	567	574	581	
625	588	595	602	609	616	623	630	637	644	650	
626	657	664	671	678	685	692	699	706	713	720	
627	727	734	741	748	754	761	768	775	782	789	
628	796	803	810	817	824	831	837	844	851	858	
629	865	872	879	886	893	900	906	913	920	927	
630	934	941	948	955	962	969	975	982	989	996	6
631	80 003	010	017	024	030	037	044	051	058	065	1 0'6
632	072	079	085	092	099	106	113	120	127	134	2 1'2
633	140	147	154	161	168	175	182	188	195	202	3 1'8
634	209	216	223	229	236	243	250	257	264	271	4 2'4
635	277	284	291	298	305	312	318	325	332	339	5 3'0
636	346	353	359	366	373	380	387	393	400	407	6 3'6
637	414	421	428	434	441	448	455	462	468	475	7 4'2
638	482	489	496	502	509	516	523	530	536	543	8 4'8
639	550	557	564	570	577	584	591	598	604	611	9 5'4
640	618	625	632	638	645	652	659	665	672	679	
641	686	693	699	706	713	720	726	733	740	747	
642	755	760	767	774	781	787	794	801	808	814	
643	821	828	835	841	848	855	862	868	875	882	
644	889	895	902	909	916	922	929	936	942	949	
645	956	963	969	976	983	990	996	003	010	017	
646	81 023	030	037	043	050	057	064	070	077	084	
647	090	097	104	111	117	124	131	137	144	151	
648	157	164	171	178	184	191	198	204	211	218	
649	224	231	238	245	251	258	265	271	278	285	

No.	Log.	0	1	2	3	4	5	6	7	8	9	Differences.
650	81	291	298	305	311	318	325	331	338	345	351	
651		358	365	371	378	385	391	398	405	411	418	
652		425	431	438	445	451	458	465	471	478	485	
653		491	498	505	511	518	525	531	538	544	551	
654		558	564	571	578	584	591	598	604	611	617	
655		624	631	637	644	651	657	664	671	677	684	
656		690	697	704	710	717	723	730	737	743	750	
657		757	763	770	776	783	790	796	803	809	816	
658		823	829	836	842	849	856	862	869	875	882	
659		889	895	902	908	915	921	928	935	941	948	
660		954	961	968	974	981	987	994	000	007	014	
661	82	020	027	033	040	046	053	060	066	073	079	
662		086	092	099	105	112	119	125	132	138	145	
663		151	158	164	171	178	184	191	197	204	210	
664		217	223	230	236	243	249	256	263	269	276	
665		282	289	295	302	308	315	321	328	334	341	
666		347	354	360	367	373	380	387	393	400	406	
667		413	419	426	432	439	445	452	458	465	471	
668		478	484	491	497	504	510	517	523	530	536	
669		543	549	556	562	569	575	582	588	595	601	
670		607	614	620	627	633	640	646	653	659	666	
671		672	679	685	692	698	705	711	718	724	730	
672		737	743	750	756	763	769	776	782	789	795	
673		802	808	814	821	827	834	840	847	853	860	
674		866	872	879	885	892	898	905	911	918	924	
675		930	937	943	950	956	963	969	975	982	988	
676		995	001	008	014	020	027	033	040	046	052	
677	83	059	065	072	078	085	091	097	104	110	117	
678		123	129	136	142	149	155	161	168	174	181	
679		187	193	200	206	213	219	225	232	238	244	
680		251	257	264	270	276	283	289	296	302	308	
681		315	321	327	334	340	347	353	359	366	372	
682		378	385	391	398	404	410	417	423	429	436	
683		442	448	455	461	467	474	480	487	493	499	
684		506	512	518	525	531	537	544	550	556	563	
685		569	575	582	588	594	601	607	613	620	626	
686		632	639	645	651	658	664	670	677	683	689	
687		696	702	708	715	721	727	734	740	746	753	
688		759	765	771	778	784	790	797	803	809	816	
689		822	828	835	841	847	853	860	866	872	879	
690		885	891	897	904	910	916	923	929	935	942	
691		948	954	960	967	973	979	985	992	998	004	
692	84	011	017	023	029	036	042	048	055	061	067	
693		073	080	086	092	098	105	111	117	123	130	
694		136	142	148	155	161	167	173	180	186	192	
695		198	205	211	217	223	230	236	242	248	255	
696		261	267	273	280	286	292	298	305	311	317	
697		323	330	336	342	348	354	361	367	373	379	
698		386	392	398	404	410	417	423	429	435	441	
699		448	454	460	466	473	479	485	491	497	504	



No.	Log.	0	1	2	3	4	5	6	7	8	9	Differences.
700	<b>84</b>	510	516	522	528	535	541	547	553	559	566	
701		572	578	584	590	597	603	609	615	621	628	
702		634	640	646	652	658	665	671	677	683	689	
703		696	702	708	714	720	726	733	739	745	751	
704		757	763	770	776	782	788	794	800	807	813	
705		819	825	831	837	844	850	856	862	868	874	
706		880	887	893	899	905	911	917	924	930	936	
707		942	948	954	960	967	973	979	985	991	997	
708	<b>85</b>	003	009	016	022	028	034	040	046	052	058	
709		065	071	077	083	089	095	101	107	114	120	
710		126	132	138	144	150	156	163	169	175	181	1 0'6
711		187	193	199	205	211	217	224	230	236	242	2 1'2
712		248	254	260	266	272	278	285	291	297	303	3 1'8
713		309	315	321	327	333	339	345	352	358	364	4 2'4
714		370	376	382	388	394	400	406	412	418	425	5 3'0
715		431	437	443	449	455	461	467	473	479	485	6 3'6
716		491	497	503	509	516	522	528	534	540	546	7 4'2
717		552	558	564	570	576	582	588	594	600	606	8 4'8
718		612	618	625	631	637	643	649	655	661	667	9 5'4
719		673	679	685	691	697	703	709	715	721	727	
720		733	739	745	751	757	763	769	775	781	787	
721		794	800	806	812	818	824	830	836	842	848	
722		854	860	866	872	878	884	890	896	902	908	
723		914	920	926	932	938	944	950	956	962	968	
724		974	980	986	992	998	004	010	016	022	028	
725	<b>86</b>	034	040	046	052	058	064	070	076	082	088	
726		094	100	106	112	118	124	130	136	141	147	
727		153	159	165	171	177	183	189	195	201	207	
728		213	219	225	231	237	243	249	255	261	267	
729		273	279	285	291	297	303	308	314	320	326	
730		332	338	344	350	356	362	368	374	380	386	5
731		392	398	404	410	415	421	427	433	439	445	1 0'5
732		451	457	463	469	475	481	487	493	499	504	2 1'0
733		510	516	522	528	534	540	546	552	558	564	3 1'5
734		570	576	581	587	593	599	605	611	617	623	4 2'0
735		629	635	641	646	652	658	664	670	676	682	5 2'5
736		688	694	700	705	711	717	723	729	735	741	6 3'0
737		747	753	759	764	770	776	782	788	794	800	7 3'5
738		806	812	817	823	829	835	841	847	853	859	8 4'0
739		864	870	876	882	888	894	900	906	911	917	9 4'5
740		923	929	935	941	947	953	958	964	970	976	
741		982	988	994	999	005	011	017	023	029	035	
742	<b>87</b>	040	046	052	058	064	070	075	081	087	093	
743		099	105	111	116	122	128	134	140	146	151	
744		157	163	169	175	181	186	192	198	204	210	
745		216	221	227	233	239	245	251	256	262	268	
746		274	280	286	291	297	303	309	315	320	326	
747		332	338	344	349	355	361	367	373	379	384	
748		390	396	402	408	413	419	425	431	437	442	
749		448	454	460	466	471	477	483	489	495	500	

No.	Log.	0	1	2	3	4	5	6	7	8	9	Differences.
750	<b>87</b>	506	512	518	523	529	535	541	547	552	558	
751		564	570	576	581	587	593	599	604	610	616	
752		622	628	633	639	645	651	656	662	668	674	
753		679	685	691	697	703	708	714	720	726	731	
754		737	743	749	754	760	766	772	777	783	789	
755		795	800	806	812	818	823	829	835	841	846	
756		852	858	864	869	875	881	887	892	898	904	
757		910	915	921	927	933	938	944	950	955	961	
758		967	973	978	984	990	996	001	007	013	018	
759	<b>88</b>	024	030	036	041	047	053	058	064	070	076	
760		081	087	093	098	104	110	116	121	127	133	G
761		138	144	150	156	161	167	173	178	184	190	1 0'6
762		195	201	207	213	218	224	230	235	241	247	2 1'2
763		252	258	264	270	275	281	287	292	298	304	3 1'8
764		309	315	321	326	332	338	343	349	355	360	4 2'4
765		366	372	377	383	389	395	400	406	412	417	5 3'0
766		423	429	434	440	446	451	457	463	468	474	6 3'6
767		480	485	491	497	502	508	513	519	525	530	7 4'2
768		536	542	547	553	559	564	570	576	581	587	8 4'8
769		593	598	604	610	615	621	627	632	638	643	9 5'4
770		649	655	660	666	672	677	683	689	694	700	
771		705	711	717	722	728	734	739	745	750	756	
772		762	767	773	779	784	790	795	801	807	812	
773		818	824	829	835	840	846	852	857	863	868	
774		874	880	885	891	897	902	908	913	919	925	
775		930	936	941	947	953	958	964	969	975	981	
776		986	992	997	003	009	014	020	025	031	037	
777	<b>89</b>	042	048	053	059	064	070	076	081	087	092	
778		098	104	109	115	120	126	131	137	143	148	
779		154	159	165	170	176	182	187	193	198	204	5
780		209	215	221	226	232	237	243	248	254	260	1 0'5
781		265	271	276	282	287	293	298	304	310	315	2 1'0
782		321	326	332	337	343	348	354	360	365	371	3 1'5
783		376	382	387	393	398	404	409	415	421	426	4 2'0
784		432	437	443	448	454	459	465	470	476	481	5 2'5
785		487	492	498	504	509	515	520	526	531	537	6 3'0
786		542	548	553	559	564	570	575	581	586	592	7 3'5
787		597	603	609	614	620	625	631	636	642	647	8 4'0
788		653	658	664	669	675	680	686	691	697	702	9 4'5
789		708	713	719	724	730	735	741	746	752	757	
790		763	768	774	779	785	790	796	801	807	812	
791		818	823	829	834	840	845	851	856	862	867	
792		873	878	883	889	894	900	905	911	916	922	
793		927	933	938	944	949	955	960	966	971	977	
794		982	988	993	998	004	009	015	020	026	031	
795	<b>90</b>	037	042	048	053	059	064	069	075	080	086	
796		091	097	102	108	113	119	124	129	135	140	
797		146	151	157	162	168	173	179	184	189	195	
798		200	206	211	217	222	227	233	238	244	249	
799		255	260	266	271	276	282	287	293	298	304	

No.	Log.	0	1	2	3	4	5	6	7	8	9	Differences.
800	90	309	314	320	325	331	336	342	347	352	358	
801		363	369	374	380	385	390	396	401	407	412	
802		417	423	428	434	439	444	450	455	461	466	
803		472	477	482	488	493	499	504	509	515	520	
804		526	531	536	542	547	553	558	563	569	574	
805		580	585	590	596	601	607	612	617	623	628	
806		634	639	644	650	655	660	666	671	677	682	
807		687	693	698	703	709	714	720	725	730	736	
808		741	747	752	757	763	768	773	779	784	789	
809		795	800	806	811	816	822	827	832	838	843	
810		848	854	859	865	870	875	881	886	891	897	
811		902	907	913	918	923	929	934	940	945	950	
812		956	961	966	972	977	982	988	993	998	004	
813	91	009	014	020	025	030	036	041	046	052	057	
814		062	068	073	078	084	089	094	100	105	110	
815		116	121	126	132	137	142	148	153	158	164	
816		169	174	180	185	190	196	201	206	212	217	
817		222	228	233	238	243	249	254	259	265	270	
818		275	281	286	291	297	302	307	312	318	323	
819		328	334	339	344	350	355	360	365	371	376	
820		381	387	392	397	403	408	413	418	424	429	
821		434	440	445	450	455	461	466	471	477	482	
822		487	492	498	503	508	514	519	524	529	535	
823		540	545	551	556	561	566	572	577	582	587	
824		593	598	603	609	614	619	624	630	635	640	
825		645	651	656	661	666	672	677	682	687	693	
826		698	703	709	714	719	724	730	735	740	745	
827		751	756	761	766	772	777	782	787	793	798	
828		803	808	814	819	824	829	834	840	845	850	
829		855	861	866	871	876	882	887	892	897	903	
830		908	913	918	923	929	934	939	944	950	955	
831		960	965	971	976	981	986	991	997	002	007	
832	92	012	018	023	028	033	038	044	049	054	059	
833		065	070	075	080	085	091	096	101	106	111	
834		117	122	127	132	137	143	148	153	158	163	
835		169	174	179	184	189	195	200	205	210	215	
836		221	226	231	236	241	247	252	257	262	267	
837		273	278	283	288	293	298	304	309	314	319	
838		324	330	335	340	345	350	355	361	366	371	
839		376	381	387	392	397	402	407	412	418	423	
840		428	433	438	443	449	454	459	464	469	474	
841		480	485	490	495	500	505	511	516	521	526	
842		531	536	542	547	552	557	562	567	572	578	
843		583	588	593	598	603	609	614	619	624	629	
844		634	639	645	650	655	660	665	670	675	681	
845		686	691	696	701	706	711	716	722	727	732	
846		737	742	747	752	758	763	768	773	778	783	
847		788	793	799	804	809	814	819	824	829	834	
848		840	845	850	855	860	865	870	875	881	886	
849		891	896	901	906	911	916	921	927	932	937	

No.	Log.	0	1	2	3	4	5	6	7	8	9	Differences.
850	<b>92</b>	942	947	952	957	962	967	973	978	983	988	
851		993	998	003	008	013	018	024	029	034	039	
852	<b>93</b>	044	049	054	059	064	069	075	080	085	090	
853		095	100	105	110	115	120	125	131	136	141	
854		146	151	156	161	166	171	176	181	186	192	
855		197	202	207	212	217	222	227	232	237	242	
856		247	252	258	263	268	273	278	283	288	293	
857		298	303	308	313	318	323	328	334	339	344	
858		349	354	359	364	369	374	379	384	389	394	
859		399	404	409	414	420	425	430	435	440	445	5
860		450	455	460	465	470	475	480	485	490	495	1 0'5
861		500	505	510	515	520	526	531	536	541	546	2 1'0
862		551	556	561	566	571	576	581	586	591	596	3 1'5
863		601	606	611	616	621	626	631	636	641	646	4 2'0
864		651	656	661	666	671	676	682	687	692	697	5 2'5
865		702	707	712	717	722	727	732	737	742	747	6 3'0
866		752	757	762	767	772	777	782	787	792	797	7 3'5
867		802	807	812	817	822	827	832	837	842	847	8 4'0
868		852	857	862	867	872	877	882	887	892	897	9 4'5
869		902	907	912	917	922	927	932	937	942	947	
870		952	957	962	967	972	977	982	987	992	997	
871	<b>94</b>	002	007	012	017	022	027	032	037	042	047	
872		052	057	062	067	072	077	082	086	091	096	
873		101	106	111	116	121	126	131	136	141	146	
874		151	156	161	166	171	176	181	186	191	196	
875		201	206	211	216	221	226	231	236	240	245	
876		250	255	260	265	270	275	280	285	290	295	
877		300	305	310	315	320	325	330	335	340	344	
878		349	354	359	364	369	374	379	384	389	394	
879		399	404	409	414	419	424	429	433	438	443	4
880		448	453	458	463	468	473	478	483	488	493	1 0'4
881		498	503	507	512	517	522	527	532	537	542	2 0'8
882		547	552	557	562	567	571	576	581	586	591	3 1'2
883		596	601	606	611	616	621	626	630	635	640	4 1'6
884		645	650	655	660	665	670	675	680	685	689	5 2'0
885		694	699	704	709	714	719	724	729	734	738	6 2'4
886		743	748	753	758	763	768	773	778	783	787	7 2'8
887		792	797	802	807	812	817	822	827	832	836	8 3'2
888		841	846	851	856	861	866	871	876	880	885	9 3'6
889		890	895	900	905	910	915	919	924	929	934	
890		939	944	949	954	959	963	968	973	978	983	
891		988	993	998	002	007	012	017	022	027	032	
892	<b>95</b>	036	041	046	051	056	061	066	071	075	080	
893		085	090	095	100	105	109	114	119	124	129	
894		134	139	143	148	153	158	163	168	173	177	
895		182	187	192	197	202	207	211	216	221	226	
896		231	236	240	245	250	255	260	265	270	274	
897		279	284	289	294	299	303	308	313	318	323	
898		328	332	337	342	347	352	357	361	366	371	
899		376	381	386	390	395	400	405	410	415	419	

No.	Log.	0	1	2	3	4	5	6	7	8	9	Differences.
900	<b>85</b>	424	429	434	439	444	448	453	458	463	468	
901		472	477	482	487	492	497	501	506	511	516	
902		521	525	530	535	540	545	550	554	559	564	
903		569	574	578	583	588	593	598	602	607	612	
904		617	622	626	631	636	641	646	650	655	660	
905		665	670	674	679	684	689	694	698	703	708	
906		713	718	722	727	732	737	742	746	751	756	
907		761	766	770	775	780	785	789	794	799	804	
908		809	813	818	823	828	832	837	842	847	852	
909		856	861	866	871	875	880	885	890	895	899	5
910		904	909	914	918	923	928	933	938	942	947	1 0'5
911		952	957	961	966	971	976	980	985	990	995	2 1'0
912		999	004	009	014	019	023	028	033	038	042	3 1'5
913	<b>96</b>	047	052	057	061	066	071	076	080	085	090	4 2'0
914		095	099	104	109	114	118	123	128	133	137	5 2'5
915		142	147	152	156	161	166	171	175	180	185	6 3'0
916		190	194	199	204	209	213	218	223	227	232	7 3'5
917		237	242	246	251	256	261	265	270	275	280	8 4'0
918		284	289	294	298	303	308	313	317	322	327	9 4'5
919		332	336	341	346	350	355	360	365	369	374	
920		379	383	388	393	398	402	407	412	417	421	
921		426	431	435	440	445	450	454	459	464	468	
922		473	478	483	487	492	497	501	506	511	515	
923		520	525	530	534	539	544	548	553	558	562	
924		567	572	577	581	586	591	595	600	605	609	
925		614	619	624	628	633	638	642	647	652	656	
926		661	666	670	675	680	685	689	694	699	703	
927		708	713	717	722	727	731	736	741	745	750	
928		753	759	764	769	774	778	783	788	792	797	
929		802	806	811	816	820	825	830	834	839	844	4
930		848	853	858	862	867	872	876	881	886	890	1 0'4
931		895	900	904	909	914	918	923	928	932	937	2 0'8
932		942	946	951	956	960	965	970	974	979	984	3 1'2
933		988	993	997	002	007	011	016	021	025	030	4 1'6
934	<b>97</b>	035	039	044	049	053	058	063	067	072	077	5 2'0
935		081	086	090	095	100	104	109	114	118	123	6 2'4
936		128	132	137	141	146	151	155	160	165	169	7 2'8
937		174	179	183	188	192	197	202	206	211	216	8 3'2
938		220	225	230	234	239	243	248	253	257	262	9 3'6
939		267	271	276	280	285	290	294	299	304	308	
940		313	317	322	327	331	336	340	345	350	354	
941		359	364	368	373	377	382	387	391	396	400	
942		405	410	414	419	424	428	433	437	442	447	
943		451	456	460	465	470	474	479	483	488	493	
944		497	502	506	511	516	520	525	529	534	539	
945		543	548	552	557	562	566	571	575	580	585	
946		589	594	598	603	607	612	617	621	626	630	
947		635	640	644	649	653	658	663	667	672	676	
948		681	685	690	695	699	704	708	713	717	722	
949		727	731	736	740	745	749	754	759	763	768	

*Five-figure Logarithms.*

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No.	Log.	0	1	2	3	4	5	6	7	8	9	Differences.
950	<b>97</b>	772	777	782	786	791	795	800	804	809	813	
951		818	823	827	832	836	841	845	850	855	859	
952		864	868	873	877	882	886	891	896	900	905	
953		909	914	918	923	928	932	937	941	946	950	
954		955	959	964	968	973	978	982	987	991	996	
955	<b>98</b>	000	005	009	014	019	023	028	032	037	041	
956		046	050	055	059	064	068	073	078	082	087	
957		091	096	100	105	109	114	118	123	127	132	
958		137	141	146	150	155	159	164	168	173	177	
959		182	186	191	195	200	204	209	214	218	223	5
960		227	232	236	241	245	250	254	259	263	268	1 0'5
961		272	277	281	286	290	295	299	304	308	313	2 1'0
962		318	322	327	331	336	340	345	349	354	358	3 1'5
963		363	367	372	376	381	385	390	394	399	403	4 2'0
964		408	412	417	421	426	430	435	439	444	448	5 2'5
965		453	457	462	466	471	475	480	484	489	493	6 3'0
966		498	502	507	511	516	520	525	529	534	538	7 3'5
967		543	547	552	556	561	565	570	574	579	583	8 4'0
968		588	592	597	601	605	610	614	619	623	628	9 4'5
969		632	637	641	646	650	655	659	664	668	673	
970		677	682	686	691	695	700	704	708	713	717	
971		722	726	731	735	740	744	749	753	758	762	
972		767	771	776	780	784	789	793	798	802	807	
973		811	816	820	825	829	834	838	843	847	851	
974		856	860	865	869	874	878	883	887	892	896	
975		900	905	909	914	918	923	927	932	936	941	
976		945	949	954	958	963	967	972	976	981	985	
977		989	994	998	003	007	012	016	021	025	029	
978	<b>99</b>	034	038	043	047	052	056	061	065	069	074	
979		078	083	087	092	096	100	105	109	114	118	4
980		123	127	131	136	140	145	149	154	158	162	1 0'4
981		167	171	176	180	185	189	193	198	202	207	2 0'8
982		211	216	220	224	229	233	238	242	247	251	3 1'2
983		255	260	264	269	273	277	282	286	291	295	4 1'6
984		300	304	308	313	317	322	326	330	335	339	5 2'0
985		344	348	352	357	361	366	370	374	379	383	6 2'4
986		388	392	396	401	405	410	414	419	423	427	7 2'8
987		432	436	441	445	449	454	458	463	467	471	8 3'2
988		476	480	484	489	493	498	502	506	511	515	9 3'6
989		520	524	528	533	537	542	546	550	555	559	
990		564	568	572	577	581	585	590	594	599	603	
991		607	612	616	621	625	629	634	638	642	647	
992		651	655	660	664	669	673	677	682	686	691	
993		695	699	704	708	712	717	721	726	730	734	
994		739	743	747	752	756	760	765	769	774	778	
995		782	787	791	795	800	804	808	813	817	822	
996		826	830	835	839	843	848	852	856	861	865	
997		870	874	878	883	887	891	896	900	904	909	
998		913	917	922	926	930	935	939	943	948	952	
999		957	961	965	970	974	978	983	987	991	996	



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